From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Assistant Commissioner for Patents
United States Patent and Trademark Office
Box PCT
Washington, D.C.20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 06 September 1999 (06.09.99)	
International application No. PCT/EP99/00441	**Applicant's or agent's file reference** 1998/F009 PCT
International filing date (day/month/year) 23 January 1999 (23.01.99)	**Priority date** (day/month/year) 04 February 1998 (04.02.98)
Applicant KREUDER, Willi et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

07 August 1999 (07.08.99)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer

F. Baechler

Telephone No.: (41-22) 338.83.38

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF THE RECORDING OF A CHANGE

(PCT Rule 92bis.1 and Administrative Instructions, Section 422)

To:

AVENTIS RESEARCH & TECHNOLOGIES
GMBH & CO. KG
Patent- und Lizenzabteilung
Gebäude K 801
D-65926 Frankfurt am Main
ALLEMAGNE

Date of mailing (day/month/year)
11 July 2000 (11.07.00)

Applicant's or agent's file reference
1998/F009 PCT

IMPORTANT NOTIFICATION

International application No.
PCT/EP99/00441

International filing date (day/month/year)
23 January 1999 (23.01.99)

1. The following indications appeared on record concerning:

[X] the applicant [ ] the inventor [ ] the agent [ ] the common representative

Name and Address
AVENTIS RESEARCH & TECHNOLOGIES
GMBH & CO. KG
D-65926 Frankfurt am Main
Germany

State of Nationality: DE
State of Residence: DE
Telephone No.: 069 305 43022
Facsimile No.: 069 305 16350
Teleprinter No.:

2. The International Bureau hereby notifies the applicant that the following change has been recorded concerning:

[ ] the person [X] the name [ ] the address [ ] the nationality [ ] the residence

Name and Address
AXIVA GMBH
D-65926 Frankfurt am Main
Germany

State of Nationality: DE
State of Residence: DE
Telephone No.: 069 305 43022
Facsimile No.: 069 305 16350
Teleprinter No.:

3. Further observations, if necessary:

4. A copy of this notification has been sent to:

[X] the receiving Office
[ ] the International Searching Authority
[ ] the International Preliminary Examining Authority
[ ] the designated Offices concerned
[X] the elected Offices concerned
[ ] other:

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No.: (41-22) 740.14.35

Authorized officer
Beatriz Morariu

Telephone No.: (41-22) 338.83.38

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION RELATING TO PRIORITY CLAIM

(PCT Rules 26bis.1 and 26bis.2 and Administrative Instructions, Sections 402 and 409)

To:

NOVO NORDISK A/S
Corporate Patents
Novo Alle
DK-2880 Bagsværd
DANEMARK

Date of mailing (day/month/year)	
20 October 1999 (20.10.99)	
Applicant's or agent's file reference	**IMPORTANT NOTIFICATION**
5654.204-WO	
International application No.	International filing date (day/month/year)
PCT/DK99/00441	17 August 1999 (17.08.99)
Applicant	
NOVO NORDISK A/S et al	

The applicant is hereby **notified** of the following in respect of the priority claim(s) made in the international application.

1. ☒ **Correction of priority claim.** In accordance with the applicant's notice received on: 18 October 1999 (18.10.99), the following priority claim has been corrected to read as follows:

DK 19 August 1998 (19.08.98) PA 1998 01044

☐ even though the indication of the number of the earlier application is missing.

☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

2. ☐ **Addition of priority claim.** In accordance with the applicant's notice received on: , the following priority claim has been added:

☐ even though the indication of the number of the earlier application is missing.

☐ even though the following indication in the priority claim is not the same as the corresponding indication appearing in the priority document:

3. ☐ As a **result of the correction and/or addition** of (a) priority claim(s) under items 1 and/or 2, the (earliest) priority date is:

4. ☐ **Priority claim considered not to have been made.**

☐ The applicant failed to respond to the Invitation under Rule 26bis.2(a) (Form PCT/IB/316) within the prescribed time limit.

☐ The applicant's notice was received after the expiration of the prescribed time limit under Rule 26bis.1(a).

☐ The applicant's notice failed to correct the priority claim so as to comply with the requirements of Rule 4.10.

The applicant may, before the technical preparations for international publication have been completed and subject to the payment of a fee, request the International Bureau to publish, together with the international application, information concerning the priority claim. See Rule 26bis.2(c) and the PCT Applicant's Guide, Volume I, Annex B2(IB).

5. ☐ In case where **multiple priorities** have been claimed, the above item(s) relate to the following priority claim(s):

6. A copy of this notification has been sent to the receiving Office and

☒ to the International Searching Authority (where the international search report has not yet been issued).

☒ the designated Offices (which have already been notified of the receipt of the record copy).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

Beate Giffo-Schmitt

Telephone No. (41-22) 338.83.38

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTICE INFORMING THE APPLICANT OF THE COMMUNICATION OF THE INTERNATIONAL APPLICATION TO THE DESIGNATED OFFICES

(PCT Rule 47.1(c), first sentence)

To:
AVENTIS RESEARCH & TECHNOLOGIES
GMBH & CO. KG
Patent- und Lizenzabteilung
Gebäude K 801
D-65926 Frankfurt am Main
ALLEMAGNE

Date of mailing (day/month/year) 12 August 1999 (12.08.99)	
Applicant's or agent's file reference 1998/F009 PCT	**IMPORTANT NOTICE**

International application No.	**International filing date** (day/month/year)	**Priority date** (day/month/year)
PCT/EP99/00441	23 January 1999 (23.01.99)	04 February 1998 (04.02.98)

Applicant
AVENTIS RESEARCH & TECHNOLOGIES GMBH & CO. KG et al

1. Notice is hereby given that the International Bureau has communicated, as provided in Article 20, the international application to the following designated Offices on the date indicated above as the date of mailing of this Notice:
   CN,EP,JP,KR,US

   In accordance with Rule 47.1(c), third sentence, those Offices will accept the present Notice as conclusive evidence that the communication of the international application has duly taken place on the date of mailing indicated above and no copy of the international application is required to be furnished by the applicant to the designated Office(s).

2. The following designated Offices have waived the requirement for such a communication at this time:
   None

   The communication will be made to those Offices only upon their request. Furthermore, those Offices do not require the applicant to furnish a copy of the international application (Rule 49.1(a-bis)).

3. Enclosed with this Notice is a copy of the international application as published by the International Bureau on
   12 August 1999 (12.08.99) under No. WO 99/40655

REMINDER REGARDING CHAPTER II (Article 31(2)(a) and Rule 54.2)

If the applicant wishes to postpone entry into the national phase until 30 months (or later in some Offices) from the priority date, **a demand for international preliminary examination** must be filed with the competent International Preliminary Examining Authority before the expiration of 19 months from the priority date.

It is the applicant's sole responsibility to monitor the 19-month time limit.

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

REMINDER REGARDING ENTRY INTO THE NATIONAL PHASE (Article 22 or 39(1))

If the applicant wishes to proceed with the international application in the **national phase**, he must, within 20 months or 30 months, or later in some Offices, perform the acts referred to therein before each designated or elected Office.

For further important information on the time limits and acts to be performed for entering the national phase, see the Annex to Form PCT/IB/301 (Notification of Receipt of Record Copy) and Volume II of the PCT Applicant's Guide.

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer
J. Zahra

Telephone No. (41-22) 338.83.38

PCT

RECEIVING OFFICE REQUEST FORM
1998/F-009 ANTRAG (5) pages

Der Unterzeichnete beantragt, daß die vorliegende internationale Anmeldung nach dem Vertrag über die internationale Zusammenarbeit auf dem Gebiet des Patentwesens behandelt wird.

Vom Anmeldeamt auszufüllen

Internationales Aktenzeichen: PCT/EP99/00541

Internationales Anmeldedatum: (23. 01. 1999)

Name des Anmeldeamts und "PCT International Application"

Aktenzeichen des Anmelders oder Anwalts *(falls gewünscht)* *(max. 12 Zeichen)*: 1998/F009 PCT

Feld Nr. I BEZEICHNUNG DER ERFINDUNG

Organic Solid State Light Sources with Narrow Band Width Emission

Feld Nr. II ANMELDER

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

Aventis Research & Technologies GmbH & Co KG

D-65926 Frankfurt am Main
Deutschland

☐ Diese Person ist gleichzeitig Erfinder

Telefonnr.: 069-305-4302

Telefaxnr.: 069-305-16350

Fernschreibnr.:

Staatsangehörigkeit (Staat): DE

Sitz oder Wohnsitz (Staat): DE

Diese Person ist Anmelder für folgende Staaten: ☐ alle Bestimmungsstaaten ☒ alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika ☐ nur die Vereinigten Staaten von Amerika ☐ die im Zusatzfeld angegebenen Staaten

Feld Nr. III WEITERE ANMELDER UND/ODER (WEITERE) ERFINDER

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

KREUDER, Willi
Sertoriusring 13
55126 Mainz
Deutschland

Diese Person ist:

☐ nur Anmelder

☒ Anmelder und Erfinder

☐ nur Erfinder *(Wird dieses Kästchen angekreuzt, so sind die nachstehenden Angaben nicht nötig.)*

Staatsangehörigkeit (Staat): DE

Sitz oder Wohnsitz (Staat): DE

Diese Person ist Anmelder für folgende Staaten: ☐ alle Bestimmungsstaaten ☐ alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika ☒ nur die Vereinigten Staaten von Amerika ☐ die im Zusatzfeld angegebenen Staaten

☒ Weitere Anmelder und/oder (weitere) Erfinder sind auf einem Fortsetzungsblatt angegeben.

Feld Nr. IV ANWALT ODER GEMEINSAMER VERTRETER; ODER ZUSTELLANSCHRIFT

Die folgende Person wird hiermit bestellt/ist bestellt worden, um für den (die) Anmelder vor den zuständigen internationalen Behörden in folgender Eigenschaft zu handeln als: ☐ Anwalt ☐ gemeinsamer Vertreter

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben.)*

Aventis Research & Technologies GmbH & Co KG
Patent- und Lizenzabteilung, Gebäude K 801
D-65926 Frankfurt am Main
Deutschland

Telefonnr.: 069-305-4302

Telefaxnr.: 069-305-16350

Fernschreibnr.:

☒ **Zustellanschrift:** Dieses Kästchen ist anzukreuzen, wenn kein Anwalt oder gemeinsamer Vertreter bestellt ist und statt dessen im obigen Feld eine spezielle Zustellanschrift angegeben ist.

Siehe Anmerkungen zu diesem Antragsformular

Fortsetzung von Feld Nr. III WEITERE ANMELDER UND/ODER (WEITERE) ERFINDER

Wird keines der folgenden Felder benutzt, so sollte dieses Blatt dem Antrag nicht beigefügt werden.

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

YU, Nu
534 Mapletree Drive
Knoxville, TN 37922
US[A]

Diese Person ist:
- [ ] nur Anmelder
- [X] Anmelder und Erfinder
- [ ] nur Erfinder *(Wird dieses Kästchen angekreuzt, so sind die nachstehenden Angaben nicht nötig.)*

Staatsangehörigkeit (Staat): CN

Sitz oder Wohnsitz (Staat): US

Diese Person ist Anmelder für folgende Staaten: [ ] alle Bestimmungsstaaten [ ] alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika [X] nur die Vereinigten Staaten von Amerika [ ] die im Zusatzfeld angegebenen Staaten

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

SALBECK, Josef
Am Flachsland 56
65779 Kelkheim
De~~utschland~~

Diese Person ist:
- [ ] nur Anmelder
- [X] Anmelder und Erfinder
- [ ] nur Erfinder *(Wird dieses Kästchen angekreuzt, so sind die nachstehenden Angaben nicht nötig.)*

Staatsangehörigkeit (Staat): DE

Sitz oder Wohnsitz (Staat): DE

Diese Person ist Anmelder für folgende Staaten: [ ] alle Bestimmungsstaaten [ ] alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika [X] nur die Vereinigten Staaten von Amerika [ ] die im Zusatzfeld angegebenen Staaten

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

Diese Person ist:
- [ ] nur Anmelder
- [ ] Anmelder und Erfinder
- [ ] nur Erfinder *(Wird dieses Kästchen angekreuzt, so sind die nachstehenden Angaben nicht nötig.)*

Staatsangehörigkeit (Staat):

Sitz oder Wohnsitz (Staat):

Diese Person ist Anmelder für folgende Staaten: [ ] alle Bestimmungsstaaten [ ] alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika [ ] nur die Vereinigten Staaten von Amerika [ ] die im Zusatzfeld angegebenen Staaten

Name und Anschrift: *(Familienname, Vorname; bei juristischen Personen vollständige amtliche Bezeichnung. Bei der Anschrift sind die Postleitzahl und der Name des Staats anzugeben. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.)*

Diese Person ist:
- [ ] nur Anmelder
- [ ] Anmelder und Erfinder
- [ ] nur Erfinder *(Wird dieses Kästchen angekreuzt, so sind die nachstehenden Angaben nicht nötig.)*

Staatsangehörigkeit (Staat):

Sitz oder Wohnsitz (Staat):

Diese Person ist Anmelder für folgende Staaten: [ ] alle Bestimmungsstaaten [ ] alle Bestimmungsstaaten mit Ausnahme der Vereinigten Staaten von Amerika [ ] nur die Vereinigten Staaten von Amerika [ ] die im Zusatzfeld angegebenen Staaten

[ ] Weitere Anmelder und/oder (weitere) Erfinder sind auf einem zusätzlichen Fortsetzungsblatt angegeben.

Feld Nr. V BESTIMMUNG VON [redacted]ATEN

Die folgenden Bestimmungen nach Regel 4.9 Absatz a werden hiermit vorgenommen *(bitte die entsprechenden Kästchen ankreuzen: wenigstens ein Kästchen muß angekreuzt werden)*:

Regionales Patent

☐ **AP** ARIPO-Patent: **GH** Ghana, **GM** Gambia, **KE** Kenia, **LS** Lesotho, **MW** Malawi, **SD** Sudan, **SZ** Swasiland, UG Uganda, **ZW** Simbabwe und jeder weitere Staat, der Vertragsstaat des Harare-Protokolls und des PCT ist

☐ **EA** Eurasisches Patent: **AM** Armenien, **AZ** Aserbaidschan, **BY** Belarus, **KG** Kirgisistan, **KZ** Kasachstan, **MD** Republik Moldau, **RU** Russische Föderation, **TJ** Tadschikistan, **TM** Turkmenistan und jeder weitere Staat, der Vertragsstaat des Eurasischen Patentübereinkommens und des PCT ist

☒ **EP** Europäisches Patent: **AT** Österreich, **BE** Belgien, **CH und LI** Schweiz und Liechtenstein, **CY** Zypern, **DE** Deutschland, **DK** Dänemark, **ES** Spanien, **FI** Finnland, **FR** Frankreich, **GB** Vereinigtes Königreich, **GR** Griechenland, **IE** Irland, **IT** Italien, **LU** Luxemburg, **MC** Monaco, **NL** Niederlande, **PT** Portugal, **SE** Schweden und jeder weitere Staat, der Vertragsstaat des Europäischen Patentübereinkommens und des PCT ist

☐ **OA** OAPI-Patent: **BF** Burkina Faso, **BJ** Benin, **CF** Zentralafrikanische Republik, **CG** Kongo, **CI** Côte d'Ivoire, **CM** Kamerun, **GA** Gabun, **GN** Guinea, **ML** Mali, **MR** Mauretanien, **NE** Niger, **SN** Senegal, **TD** Tschad, **TG** Togo und jeder weitere Staat, der Vertragsstaat der OAPI und des PCT ist *(falls eine andere Schutzrechtsart oder ein sonstiges Verfahren gewünscht wird, bitte auf der gepunkteten Linie angeben)* .....

Nationales Patent *(falls eine andere Schutzrechtsart oder ein sonstiges Verfahren gewünscht wird, bitte auf der gepunkteten Linie angeben):*

☐ **AL** Albanien .....
☐ **AM** Armenien .....
☐ **AT** Österreich .....
☐ **AU** Australien .....
☐ **AZ** Aserbaidschan
☐ **BA** Bosnien-Herzegowina .....
☐ **BB** Barbados
☐ **BG** Bulgarien .....
☐ **BR** Brasilien .....
☐ **BY** Belarus .....
☐ **CA** Kanada
☐ **CH und LI** Schweiz und Liechtenstein
☒ **CN** China .....
☐ **CU** Kuba .....
☐ **CZ** Tschechische Republik .....
☐ **DE** Deutschland .....
☐ **DK** Dänemark .....
☐ **EE** Estland .....
☐ **ES** Spanien .....
☐ **FI** Finnland .....
☐ **GB** Vereinigtes Königreich
☐ **GE** Georgien .....
☐ **GH** Ghana .....
☐ **GM** Gambia
☐ **GW** Guinea-Bissau .....
☐ **HR** Kroatien
☐ **HU** Ungarn .....
☐ **ID** Indonesien
☐ **IL** Israel .....
☐ **IS** Island
☒ **JP** Japan .....
☐ **KE** Kenia .....
☐ **KG** Kirgisistan .....
☐ **KP** Demokratische Volksrepublik Korea .....
☐ .....
☒ **KR** Republik Korea .....
☐ **KZ** Kasachstan .....
☐ **LC** Saint Lucia
☐ **LK** Sri Lanka
☐ **LR** Liberia
☐ **LS** Lesotho .....
☐ **LT** Litauen
☐ **LU** Luxemburg
☐ **LV** Lettland
☐ **MD** Republik Moldau .....
☐ **MG** Madagaskar .....
☐ **MK** Die ehemalige jugoslawische Republik Mazedonien .....
☐ **MN** Mongolei
☐ **MW** Malawi .....
☐ **MX** Mexiko .....
☐ **NO** Norwegen
☐ **NZ** Neuseeland .....
☐ **PL** Polen .....
☐ **PT** Portugal .....
☐ **RO** Rumänien
☐ **RU** Russische Föderation .....
☐ **SD** Sudan
☐ **SE** Schweden
☐ **SG** Singapur
☐ **SI** Slowenien .....
☐ **SK** Slowakei .....
☐ **SL** Sierra Leone
☐ **TJ** Tadschikistan .....
☐ **TM** Turkmenistan .....
☐ **TR** Türkei .....
☐ **TT** Trinidad und Tobago .....
☐ **UA** Ukraine .....
☐ **UG** Uganda .....
☒ **US** Vereinigte Staaten von Amerika .....
☐ **UZ** Usbekistan .....
☐ **VN** Vietnam .....
☐ **YU** Jugoslawien .....
ZW Simbabwe .....

Kästchen für die Bestimmung von Staaten (für die Zwecke eines nationalen Patents), die dem PCT nach der Veröffentlichung dieses Formblatts beigetreten sind:

☐ GD Grenada .....
☐ IN Indien .....

Erklärung bzgl. vorsorglicher Bestimmungen: Zusätzlich zu den oben genannten Bestimmungen nimmt der Anmelder nach Regel 4.9 Absatz b auch alle anderen nach dem PCT zulässigen Bestimmungen vor mit Ausnahme der im Zusatzfeld genannten Bestimmungen, die von dieser Erklärung ausgenommen sind. Der Anmelder erklärt, daß diese zusätzlichen Bestimmungen unter dem Vorbehalt einer Bestätigung stehen und jede zusätzliche Bestimmung, die vor Ablauf von 15 Monaten ab dem Prioritätsdatum nicht bestätigt wurde, nach Ablauf dieser Frist als vom Anmelder zurückgenommen gilt. *(Die Bestätigung einer Bestimmung erfolgt durch die Einreichung einer Mitteilung, in der diese Bestimmung angegeben wird, und die Zahlung der Bestimmungs- und der Bestätigungsgebühr. Die Bestätigung muß beim Anmeldeamt innerhalb der Frist von 15 Monaten eingehen.)*

Feld Nr. VI PRIORITÄTSANSPRUCH ☐ Weitere Prioritätsansprüche sind im Zusatzfeld angegeben.

Anmeldedatum der früheren Anmeldung *(Tag/Monat)*	Aktenzeichen der früheren Anmeldung	Ist die frühere Anmeldung eine: national Anmeldung: Staat	regionale Anmeldung:* regionales Amt	internationale Anmeldung: Anmeldeamt
Zeile (1) 04. Februar 1998 (04.02.98)	98101902.9	EP		
Zeile (2)				
Zeile (3)				

☐ Das Anmeldeamt wird ersucht, eine beglaubigte Abschrift der oben in der (den) Zeile(n) _____ bezeichneten früheren Anmeldung(en) zu erstellen und dem internationalen Büro zu übermitteln *(nur falls die frühere Anmeldung(en) bei dem Amt eingereicht worden ist(sind), das für die Zwecke dieser internationalen Anmeldung Anmeldeamt ist)*

** Falls es sich bei der früheren Anmeldung um eine ARIPO-Anmeldung handelt, so muß in dem Zusatzfeld mindestens ein Staat angegeben werden, der Mitgliedstaat der Pariser Verbandsübereinkunft zum Schutz des gewerblichen Eigentums ist und für den die frühere Anmeldung eingereicht wurde.*

Feld Nr. VII INTERNATIONALE RECHERCHENBEHÖRDE

Wahl der internationalen Recherchenbehörde (ISA) *(falls zwei oder mehr als zwei internationale Recherchenbehörden für die Ausführung der internationalen Recherche zuständig sind, geben Sie die von Ihnen gewählte Behörde an; der Zweibuchstaben-Code kann benutzt werden)*

ISA /

Antrag auf Nutzung der Ergebnisse einer früheren Recherche; Bezugnahme auf diese frühere Recherche *(falls eine frühere Recherche bei der internationalen Recherchenbehörde beantragt oder von ihr durchgeführt worden ist):*

Datum *(Tag/Monat/Jahr)* Aktenzeichen Staat *(oder regionales Amt)*

Feld Nr. VIII KONTROLLISTE; EINREICHUNGSSPRACHE

Diese internationale Anmeldung enthält die folgende **Anzahl von Blättern:**

Antrag	: 4
Beschreibung (ohne Sequenzprotokollteil)	: 30
Ansprüche	: 7
Zusammenfassung	: 1
Zeichnungen	:
Sequenzprotokollteil der Beschreibung	:
Blattzahl insgesamt	: 42

Dieser internationalen Anmeldung **liegen** die nachstehend angekreuzten Unterlagen **bei:**

1. ☒ Blatt für die Gebührenberechnung
2. ☐ Gesonderte unterzeichnete Vollmacht
3. ☐ Kopie der allgemeinen Vollmacht; Aktenzeichen (falls vorhanden):
4. ☐ Begründung für das Fehlen einer Unterschrift
5. ☐ Prioritätsbeleg(e), in Feld Nr. VI durch folgende Zeilennummer gekennzeichnet:
6. ☐ Übersetzung der internationalen Anmeldung in die folgende Sprache:
7. ☐ Gesonderte Angaben zu hinterlegten Mikroorganismen oder anderem biologischen Material
8. ☐ Sequenzprotokolle für Nucleotide und/oder Aminosäuren in computerlesbarer Form
9. ☐ Sonstige *(einzeln aufführen):*

Abbildung der Zeichnungen, die mit der Zusammenfassung veröffentlicht werden soll (Nr.):

Sprache, in der die internationale Anmeldung eingereicht wird: englisch

Feld Nr. IX UNTERSCHRIFT DES ANMELDERS ODER DES ANWALTS

Der Name jeder unterzeichnenden Person ist neben der Unterschrift zu wiederholen, und es ist anzugeben, sofern sich dies nicht eindeutig aus dem Antrag ergibt, in welcher Eigenschaft die Person unterzeichnet.

Aventis Research & Technologies GmbH & Co KG

ppa. Ackermann i.V. Dr. Dörr

Vom Anmeldeamt auszufüllen

1. Datum des tatsächlichen Eingangs dieser internationalen Anmeldung: 23 JAN 1999 (23. 01. 99)
2. Zeichnungen ☐ eingegangen: ☐ nicht eingegangen:
3. Geändertes Eingangsdatum aufgrund nachträglich, jedoch fristgerecht eingegangener Unterlagen oder Zeichnungen zur Vervollständigung dieser internationalen Anmeldung:
4. Datum des fristgerechten Eingangs der angeforderten Richtigstellungen nach Artikel 11(2) PCT:
5. Internationale Recherchenbehörde *(falls zwei oder mehr zuständig sind)*: ISA /
6. ☐ Übermittlung des Recherchenexemplars bis zur Zahlung der Recherchengebühr aufgeschoben

Vom Internationalen Büro auszufüllen

Datum des Eingangs des Aktenexemplars beim Internationalen Büro:

Zusatzfeld *Wird dieses Zusatzfeld nicht benutzt, so ist dieses Blatt dem Antrag nicht beizufügen.*

Dieses Feld ist in folgenden Fällen auszufüllen:

1. Wenn der Platz in einem Feld nicht für alle Angaben ausreicht:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. ..." [Nummer des Feldes angeben] die gleichen Angaben zu machen wie in dem Feld vorgesehen, das platzmäßig nicht ausreicht;*
insbesondere:	
i) Wenn mehr als zwei Anmelder und/oder Erfinder vorhanden sind und kein Fortsetzungsblatt zur Verfügung steht:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. III" für jede weitere Person die in Feld Nr. III vorgesehenen Angaben zu machen. Der in diesem Feld in der Anschrift angegebene Staat ist der Staat des Sitzes oder Wohnsitzes des Anmelders, sofern nachstehend kein Staat des Sitzes oder Wohnsitzes angegeben ist.*
ii) Wenn in Feld Nr. II oder III die Angabe "die im Zusatzfeld angegebenen Staaten" angekreuzt ist:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. II", "Fortsetzung von Feld Nr. III" oder "Fortsetzung von Feld Nr. II und Nr. III" die Namen der Anmelder und neben jedem Namen der Staat oder die Staaten (und/oder ggf. ARIPO-, eurasisches, europäisches oder OAPI-Patent) anzugeben, für die die bezeichnete Person Anmelder ist.*
iii) Wenn der in Feld Nr. II oder III genannte Erfinder oder Erfinder/Anmelder nicht für alle Bestimmungsstaaten oder für die Vereinigten Staaten von Amerika als Erfinder benannt ist:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. II" oder "Fortsetzung von Feld Nr. III" oder "Fortsetzung von Feld Nr. II und Nr. III" der Name des Erfinders und neben jedem Namen der Staat oder die Staaten (und/oder ggf. ARIPO-, eurasisches, europäisches oder OAPI-Patent) anzugeben, für die die bezeichnete Person Erfinder ist.*
iv) Wenn zusätzlich zu dem Anwalt/den Anwälten, die in Feld Nr. IV angegeben sind, weitere Anwälte bestellt sind:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. IV" für jeden weiteren Anwalt die gleichen Angaben zu machen wie in Feld Nr. IV vorgesehen.*
v) Wenn in Feld Nr. V bei einem Staat (oder bei OAPI) die Angabe "Zusatzpatent" oder "Zusatzzertifikat" oder wenn in Feld Nr. V bei den Vereinigten Staaten von Amerika die Angabe "Fortsetzung" oder "Teilfortsetzung" hinzugefügt wird:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. V" die Namen der betreffenden Staaten (oder OAPI) und nach dem Namen jeder dieser Staaten (oder OAPI) das Aktenzeichen des Hauptschutzrechts oder der Hauptschutzrechtsanmeldung und das Datum der Erteilung des Hauptschutzrechts oder der Einreichung der Hauptschutzrechtsanmeldung anzugeben.*
vi) Wenn die Priorität von mehr als drei früheren Anmeldungen beansprucht wird:	*In diesem Fall sind mit dem Vermerk "Fortsetzung von Feld Nr. VI" für jede weitere frühere Anmeldung die gleichen Angaben zu machen wie in Feld Nr. VI vorgesehen.*
2. Wenn der Anmelder für irgendein Bestimmungsamt die Vergünstigung nationaler Vorschriften betreffend unschädliche Offenbarung oder Ausnahmen von der Neuheitsschädlichkeit in Anspruch nimmt:	***In diesem Fall ist mit dem Vermerk "Erklärung betreffend unschädliche Offenbarung oder Ausnahmen von der Neuheitsschädlichkeit" nachstehend diese Erklärung abzugeben.***

Feld Nr. IX. Unterschrift des Anmelder oder des Anwalts

Willi Kreuder

Willi Kreuder

Nu Yu

Josef Salbeck

Josef Salbeck

50 Co 09/582952 1621

PATENT COOPERATION TREATY

RECD 27 JUN 2000

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 5367-PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US99/00475	International filing date *(day/month/year)* 09 JANUARY 1999	Priority date *(day/month/year)* 09 JANUARY 1998
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant ARIZONA BOARD OF REGENTS		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 4 sheets.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

   I ☒ Basis of the report

   II ☐ Priority

   III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability

   IV ☐ Lack of unity of invention

   V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

   VI ☐ Certain documents cited

   VII ☐ Certain defects in the international application

   VIII ☐ Certain observations on the international application

RECEIVED
OCT 02 2000
TECH CENTER 1600/2900

Date of submission of the demand	Date of completion of this report
09 AUGUST 1999	24 APRIL 2000
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer SREENI PADMANABHAN Telephone No. (703) 308-1235

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/00475

I. Basis of the report

1. With regard to the **elements** of the international application:*

[X] the international application as originally filed

[X] the description:
pages 1-29, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____

[X] the claims:
pages 1-5, as originally filed
pages NONE, as amended (together with any statement) under Article 19
pages NONE, filed with the demand
pages NONE, filed with the letter of _____

[X] the drawings:
pages 1-5, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____

[X] the sequence listing part of the description:
pages NONE, as originally filed
pages NONE, filed with the demand
pages NONE, filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

[ ] contained in the international application in printed form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. [X] The amendments have resulted in the cancellation of:

[X] the description, pages NONE

[X] the claims, Nos. NONE

[X] the drawings, sheets/fig NONE

5. [X] This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

Form PCT/IPEA/409 (Box I) (July 1998)

Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US99/00475

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	NONE	YES
	Claims	1-5	NO
Inventive Step (IS)	Claims	1-2 and 4-5	YES
	Claims	3	NO
Industrial Applicability (IA)	Claims	1-5	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-5 lack novelty under PCT Article 33(2) as being anticipated by Cushman et al. (US patent No. 5,430,062).

Cushman discloses phenstatin compounds and derivatives claimed in the instant invention (see for example compound 27, columns 19-20). Cushman also teaches the use of these compounds as anti-cancer drugs.

Claim 3 lacks an inventive step under PCT Article 33(3) as being obvious over Pettit et al. (US patent No. 4,996,237).

Pettit teaches the use of similar compounds, combrestatins, for the inhibition of cancer cell growth and tubulin polymerization. Such a teaching renders the applicants teaching of similar phensatin prodrugs an obvious extrapolation of Pettit's teachings.

Claims 1-2 and 4-5 meet the criteria set under PCT Article 33(3).

Claims 1-5 meet the criteria set out under PCT Article 33(4).

---------- NEW CITATIONS ----------

NONE

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(6): A61K 31/09, 31/075, 31/66; C07C 43/215, 217/80 and US Cl.: 514/646, 720, 130, 721; 568/331, 332, 631, 646

I. BASIS OF REPORT:

5. (Some) amendments are considered to go beyond the disclosure as filed:
NONE

M·H

5

PATENT COOPERATION TREATY

REC'D 24 FEB 2000
WIPO PCT

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
1998/F009 PCT		
International application No.	International filing date *(day/month/year)*	Priority date *(day/month/year)*
PCT/EP99/00441	23/01/1999	04/02/1998
International Patent Classification (IPC) or national classification and IPC H01S3/16		
Applicant AVENTIS RESEARCH & TECHNOLOGIES GMBH & CO. KG		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 1 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations suporting such statement
   - VI ☐ Certain documents cited
   - VII ☒ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
07/08/1999	22.02.2000
Name and mailing address of the international preliminary examining authority: European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Ketterl, F Telephone No. +49 89 2399 2467

Form PCT/IPEA/409 (cover sheet) (January 1994)

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP99/00441

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

Description, pages:

1-30	as originally filed				

Claims, No.:

3 (part),4	as originally filed				
1,2,3 (part)	as received on	20/01/2000	with letter of	20/01/2000	

2. The amendments have resulted in the cancellation of:

☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-4
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-4
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-4
	No:	Claims	

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

CONCERNING SECTION V:

1). The use according to claim 1 involves an inventive step and therefore, the requirements of Article 33 (2) to (4) PCT are met. The reasons are as follows:

As the closest prior art reference, EP,A,0 676 461 (hereinafter referred to as D1) has to be taken into account. From this document, there is known (see e.g. the abstract) the use of spiro compounds of formula (I) as electroluminescent dyes.

In claim 1, a different use of these spiro compounds, namely, as a solid laser dye, is claimed. The problem to be solved can therefore be seen in adding a further use of the spiro compounds of formula (i) to the use known from D1.

The solution involves an inventive step. Although the use of **solutions** of dyes of a similar structure as laser dyes is known, see e.g. DE,A,37 03 065 (hereinafter referred to as D2; see claim 8) or the Liphart et al. article "Bifluorophore Laserfarbstoffe zur Steigerung des Wirkungsgrades von Farbstofflasern" from Liebigs Ann. Chem. 1981, 1118-1138 (hereinafter referred to as D3; see e.g. pages 1123 to 1124), it cannot be extrapolated that spiro compounds as defined in claim 1 can be used as **solid** laser dyes. Hence the claimed use is not rendered obvious by the cited prior art.

1.1 Claims 2 to 4 refer to embodiments of the use defined in claim 1. Hence the subject-matter of these claims likewise involves an inventive step, and therefore, the requirements of Article 33 (2) to (4) PCT are met.

CONCERNING SECTION VII:

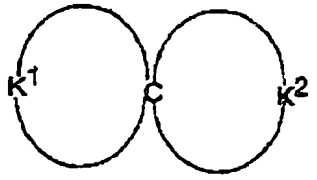
1). Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in the documents D2 and D3 is not mentioned in the description, nor are these documents identified therein.

2). The description is not brought into conformity with the claims as required by Rule 5.1(a)(iii) PCT.

3). As regards the reference to other documents on page 11, lines 5 to 8, it has to be taken into account that the description should, with respect to the essential features of the invention, be capable of being understood without reference to any other document. Therefore, there is doubt whether matter in this document is essential to satisfy the requirements of Article 5 PCT. If this is the case, such matter should expressely be incorporated into the description. Otherwise, the expression "the disclosure of which is incorporated herein by reference" should be deleted. Further, the document is not identified in such a manner that it can be easily retrieved, see PCT International Preliminary Examination Guidelines II-4.17.

Claims:

1. Use of spiro compounds of the formula (I)

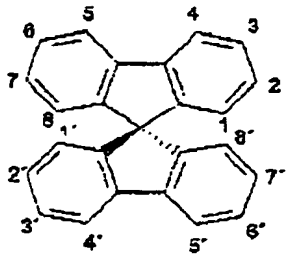


(I)

where

K^1 and K^2 are, independently of one another, conjugated systems, as a solid laser dye.

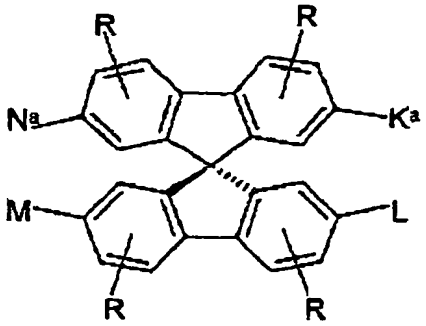
2. Use as claimed in claim 1, wherein the spiro compound used is a spirobifluorene of the formula (II)



(II)

where the benzo groups can be substituted and/or fused independently of one another.

3. Use as claimed in claim 1 and/or 2, wherein use is made of a spirobifluorene derivative of the formula (III)



(III)

where the symbols and indices have the following meaning:

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION** see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
1998/F009 PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/EP 99/ 00441	23/01/1999	04/02/1998
Applicant		
AVENTIS RESEARCH & TECHNOLOGIES GMBH & CO. KG		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [ ] the text is approved as submitted by the applicant.

   [X] the text has been established by this Authority to read as follows:

   USE OF SPIRO COMPOUNDS AS LASER DYES

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. ---

   [ ] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
EP 99/00441

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01S3/16 H01S3/213 C09B57/00 //C07C13/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01S C09B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 676 461 A (HOECHST AG) 11 October 1995 see page 3, line 32 - line 57; claims 1-5 ---	1-4
Y	LIPHARDT B ET AL: "LASERFARBSTOFFE, I. BIFLUOROPHORE LASERFARBSTOFFE ZUR STEIGERUNG DES WIRKUNGSGRADES VON FARBSTOFF-LASERN LASER DYES, I. BIFLUOROPHORIC LASER DYES FOR INCREASE OF THE EFFICIENCY OF DYE LASERS" LIEBIGS ANNALEN DER CHEMIE, vol. 1981, no. 6, June 1981, pages 1118-1138, XP002030899 * abstract * --- -/--	1-4

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 May 1999	25/05/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ginoux, C

1

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International Application No
EP 99/00441

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	SUTCLIFFE F K ET AL: "THE SYNTHESIS AND PROPERTIES OF DYES AND PIGMENTS CONTAINING A 9,9'-SPIROBIFLUORENE RESIDUE" JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, vol. 94, no. 7, July 1978, pages 306-309, XP002030898 cited in the application * Experimental part *	1-4
A	US 5 149 807 A (HAMMOND PETER R ET AL) 22 September 1992 see column 1, line 16 - line 68; claims; examples	1-4
A	DE 37 03 065 A (EXCITON CHEMICAL CO) 20 August 1987 see claims 1-14,25-30; examples 1,2	1-4
A	US 3 781 711 A (DREXHAGE K ET AL) 25 December 1973 see column 3, line 48 - column 4, line 49; claims	1-4

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/00441

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0676461 A	11-10-1995	DE 4411969 A	19-10-1995
		DE 4442063 A	30-05-1996
		DE 4446818 A	04-07-1996
		CN 1112951 A	06-12-1995
		JP 7278537 A	24-10-1995
		US 5840217 A	24-11-1998
US 5149807 A	22-09-1992	NONE	
DE 3703065 A	20-08-1987	JP 62260883 A	13-11-1987
		US 5041238 A	20-08-1991
		US 5037578 A	06-08-1991
US 3781711 A	25-12-1973	DE 2351142 A	02-05-1974
		FR 2202920 A	10-05-1974
		JP 49074895 A	19-07-1974

USE OF SPIRO COMPOUNDS AS LASER DYES

Willi Kreuder
Nu Yu
-and-
Josef Salbeck

COPY OF
INTERNATIONAL APPLICATION
(ENGLISH)
including Search Report

PCT/EP99/00441 .... IFD: 01/23/99

1998/F-009 .... (7266*40)

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 :
H01S 3/16, 3/213, C09B 57/00 // C07C 13/72

A1

(11) International Publication Number: WO 99/40655

(43) International Publication Date: 12 August 1999 (12.08.99)

(21) International Application Number: PCT/EP99/00441

(22) International Filing Date: 23 January 1999 (23.01.99)

(30) Priority Data:
98101902.9 4 February 1998 (04.02.98) EP

(71) Applicant *(for all designated States except US)*: AVENTIS RESEARCH & TECHNOLOGIES GMBH & CO. KG [DE/DE]; D–65926 Frankfurt am Main (DE).

(72) Inventors; and
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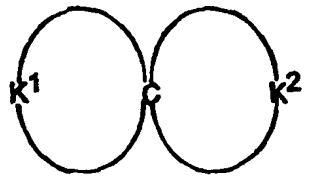
(54) Title: USE OF SPIRO COMPOUNDS AS LASER DYES

(57) Abstract

Use of spiro compounds of formula (I), where K^1 and K^2 are, independently of one another, conjugated systems, as a laser dye.



(I)

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Description

USE OF SPIRO COMPOUNDS AS LASER DYES

Narrow band width emission of organic dyes in dilute solution is a well known phenomena with so called laser dyes. [for an overview see for example: R.Raue, Laser Dyes, in Ullmann's Encyclopedia of Industrial Chemistry, 5.Ed.] In such an arrangement the dye laser employs a dilute solution of a fluorescent dye. The dye solution is contained in a thin-walled quartz cell, which forms part of a closed system, through which the solution is circulated while the laser is in operation. The active medium may also take the form of a liquid stream, emitted from a jet, that crosses the laser cavity perpendicular to the optical axis. Excitation of the dye is achieved by means of so-called optical pumping, using a source of energy such as a flash lamp ; the dye laser can also be stimulated by a gas laser, such as a nitrogen, argon, or krypton laser. The excimer (i.e., excited dimer) laser is frequently used as pumping light source, particularly the xenon chloride or krypton fluoride laser. Laser dyes include a large number of long-known fluorescent compounds, other representatives are optical brighteners and fluorescent dyes. In this case, only solutions of the common laser dyes in a suitable solvent can be used.

Therefore there are many attempts to prepare solid state devices with organic emitters. In that case, solid solutions of organic dyes in a suitable solid matrix, have been applied.

For example using sol-gel processes with organically modified silicates or optically transparent polymers as matrix have been applied [W.Hu, et al. Appl.Opt. 36 (1997) 579; R.Reisfeld, Proc.SPIE-Int.Soc.Opt.Eng. 2288 (1994) 563; S.E.Friberg, et al. J.Mater.Synth.Process. 2 (1994) 29; C.Whitehurst, et al. Proc.SPIE-int.Soc.Opt.Eng. 1328 (1990) 183].

But in all cases only low concentrations of the laser dye in the matrix can be applied due to quenching processes at higher concentrations. Another problem is the limited photo stability of most of the applied laser dyes.

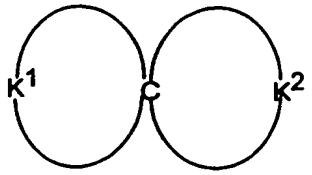
Very recently, conjugated polymers have been described as a new class of solid-state laser materials. In this case the lasing is evidenced by a dramatic collapse of the emission line width to as little as 7 nm. [M.A. Diaz-Garcia, et al. Synth.Met. 84 (1997) 455; N.Tessler, Synth.Met. 84 (1997) 475; S.V.Frolov, et al. Synth.Met. 84 (1997) 471, 473.]

More recently, vacuum deposited thin films of tris-(8-hydroxyquinoline)aluminium (Alq_3) doped with 2.5 % of a DCM laser dye have been described to show laser action [V.G.Kozlov, et al. Nature 389 (1997) 362]. Using cascade energy transfer to obtain stimulated emission, low molecular host guest systems containing a combination of low concentrations of different laser dyes (of the order of 1%) in a 2-(4-biphenylyl)-5-(4-*t*-butylphenyl)-1,3,4-oxadiazole (PBD) host has been described [M. Berggren, et al. Nature 389 (1997) 466]; in this paper also the amplifying characteristics of a neat PBD film has been described.

But the low molecular weight systems described suffer from the low (thermal and) morphologic stability, which is required for a stable emission over time.

Surprisingly, it was found that a special class of low molecular organic compounds based on spiro compounds are exceptionally well qualified as active materials in organic solid state light sources with narrow band width emission. Both, in the neat state as well as acting as an host in combination with small amounts of laser dyes. Narrow band width emissions means that the free width at half maximum (FWHM) is equal or below 10 nm.

The invention accordingly provides for the use of spiro compounds of the formula (I)



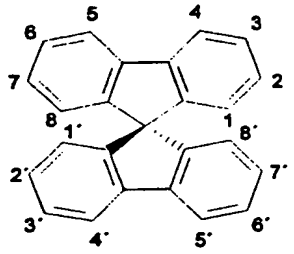
(I)

where

K^1 and K^2 are, independently of one another, conjugated systems, as laser dyes.

Compounds of the formula (I) are readily soluble in customary organic solvents, have improved film-forming properties and have a significantly reduced tendency to crystallize. This makes the production of organic laser devices easier and increases their service life.

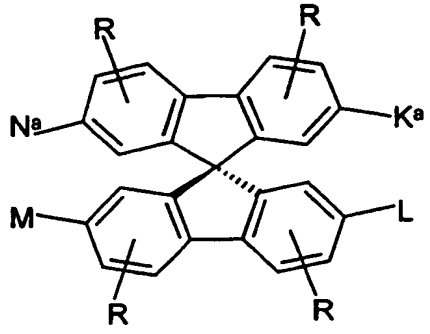
Preferred compounds of the formula (I) are 9,9'-spiro-bifluorene derivatives of the formula (II),



(II)

where the benzo groups can be substituted and/or fused independently of one another.

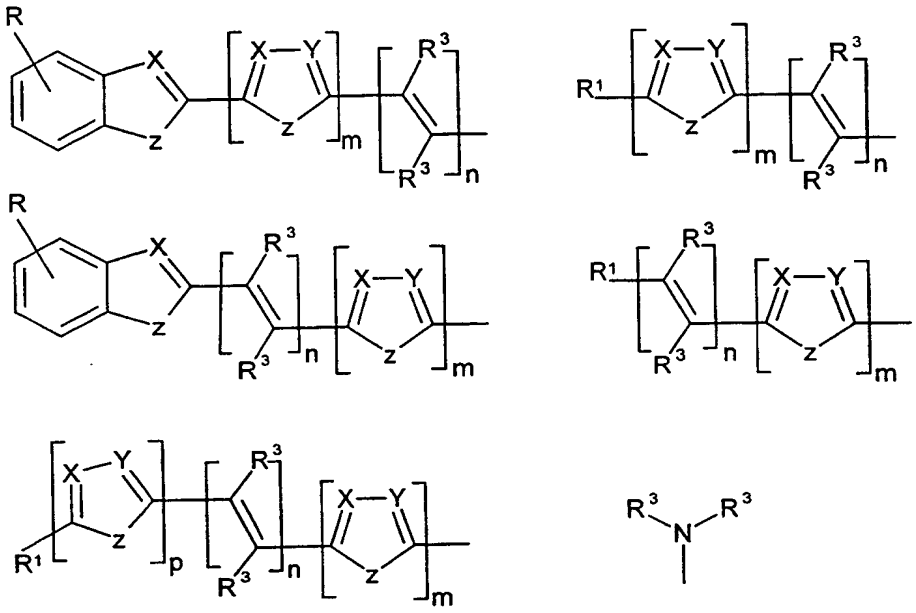
Particular preference is given to spirobifluorene derivatives of the formula (III)



(III)

where the symbols and indices have the following meanings:

K^a, L, M, N^a are identical or different and are



R can be identical or different an each appearance and have the same meanings as K^a, L, M, N^a or is H, a linear or branched alkyl, alkoxy or ester group having from 1 to 22, preferably from 1 to 15, particularly preferably from 1 to 22, carbon atoms, -CN, $-NO_2$, $-NR^2R^3$, -Ar- or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furyl, with each of these groups being able to bear one or two radicals R,

m, n, p are 0, 1, 2 or 3;

X, Y are identical or different and are CR or nitrogen;

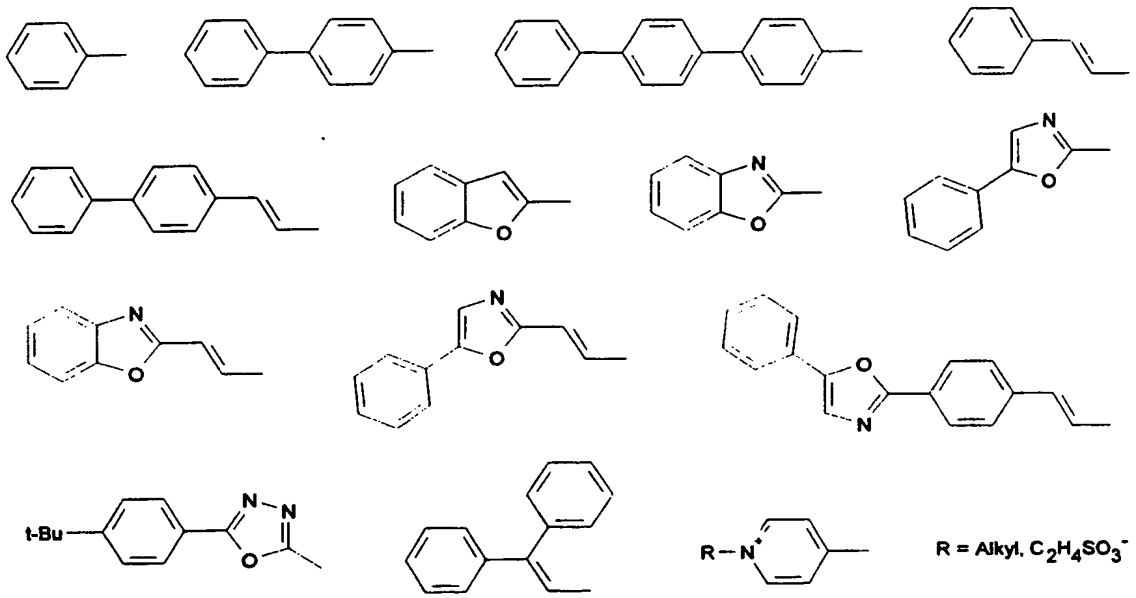
Z is -O-, -S- $-NR^1$-, $-CR^1R^4$-, -CH=CH-, -CH=N-;

R^1, R^4 can be identical or different and have the same meanings as R;

R^2, R^3 are identical or different and are H, a linear or branched alkyl group having from 1 to 22 carbon atoms, -Ar, 3-methylphenyl.

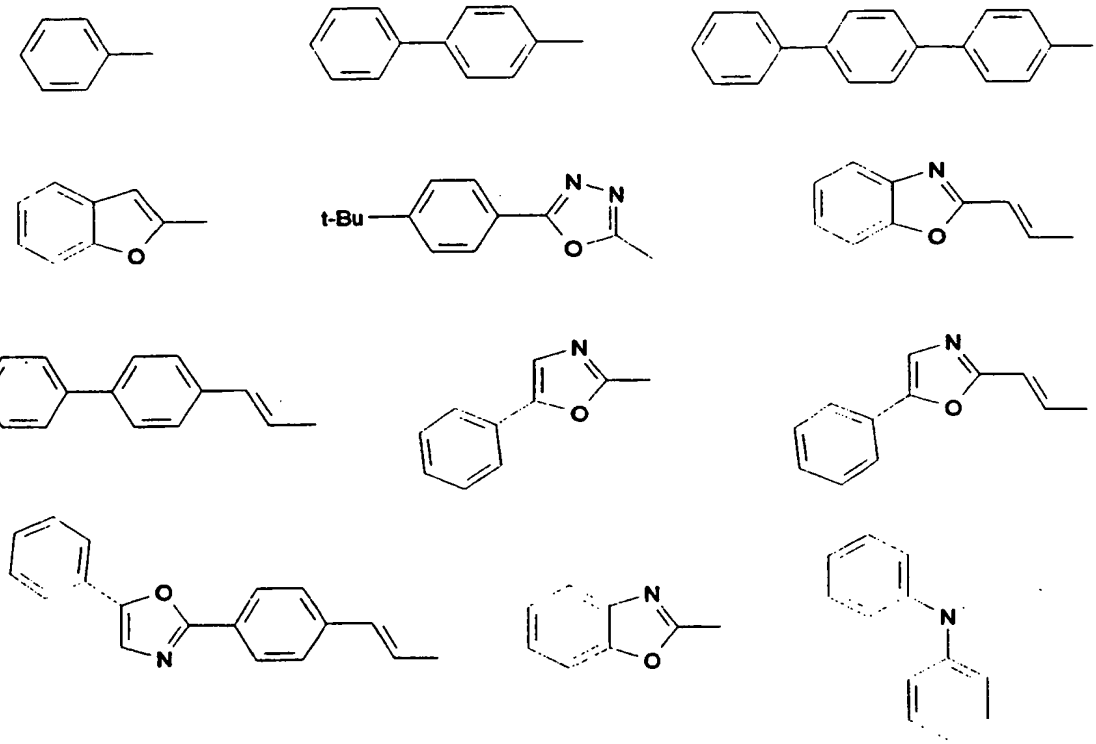
Preferred compounds of the formula (III) are those of the formulae (IIIa) - (IIIg)

IIIa) K^a = L = M = N^a and is selected from the group consisting of:

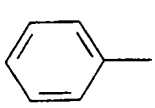
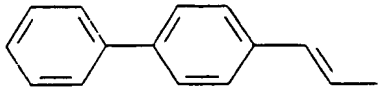
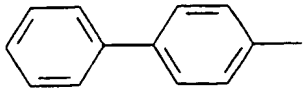
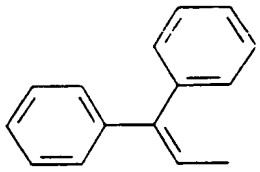
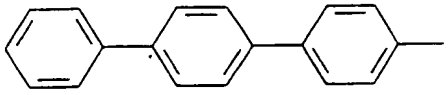
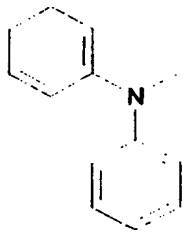
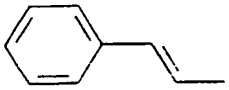
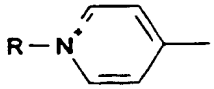


R = C_1-C_{22}-Alkyl, $C_2H_4SO_3$-

IIIb) K^a = M = H and N^a = L and is selected from the group consisting of:

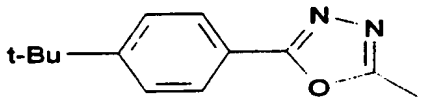
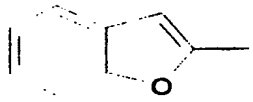
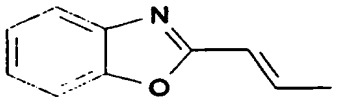
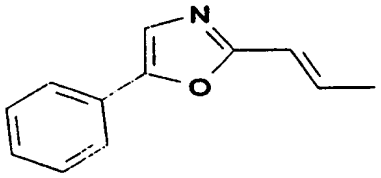
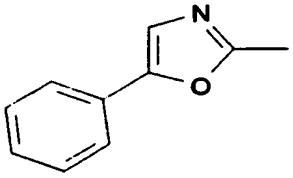
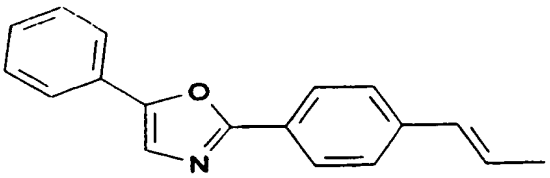
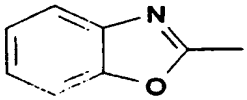


IIIc) K^a = M and is selected from the group consisting of:

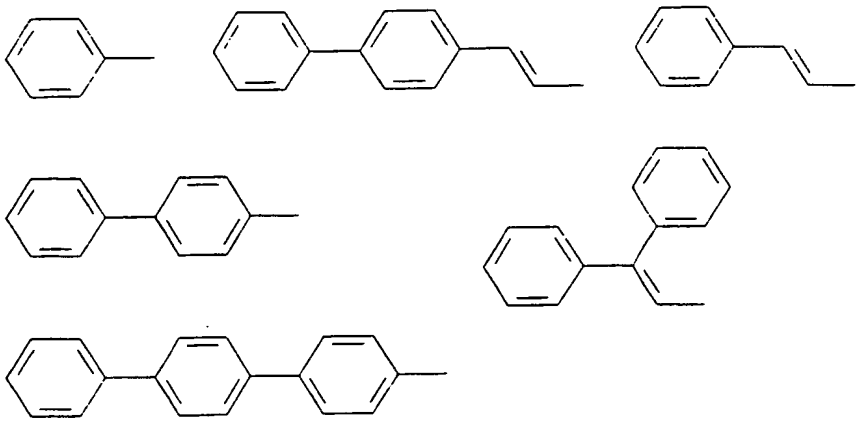









R = Alkyl, $C_2H_4SO_3^-$

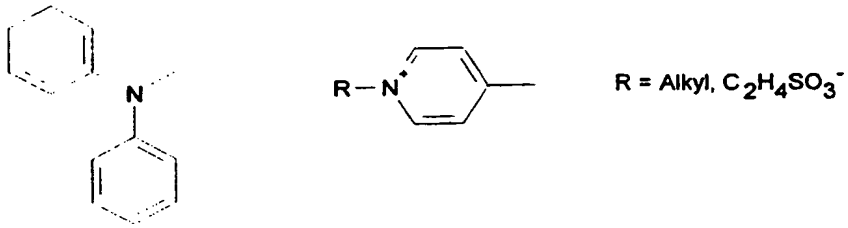
and N^a = L and is selected from the group consisting of:

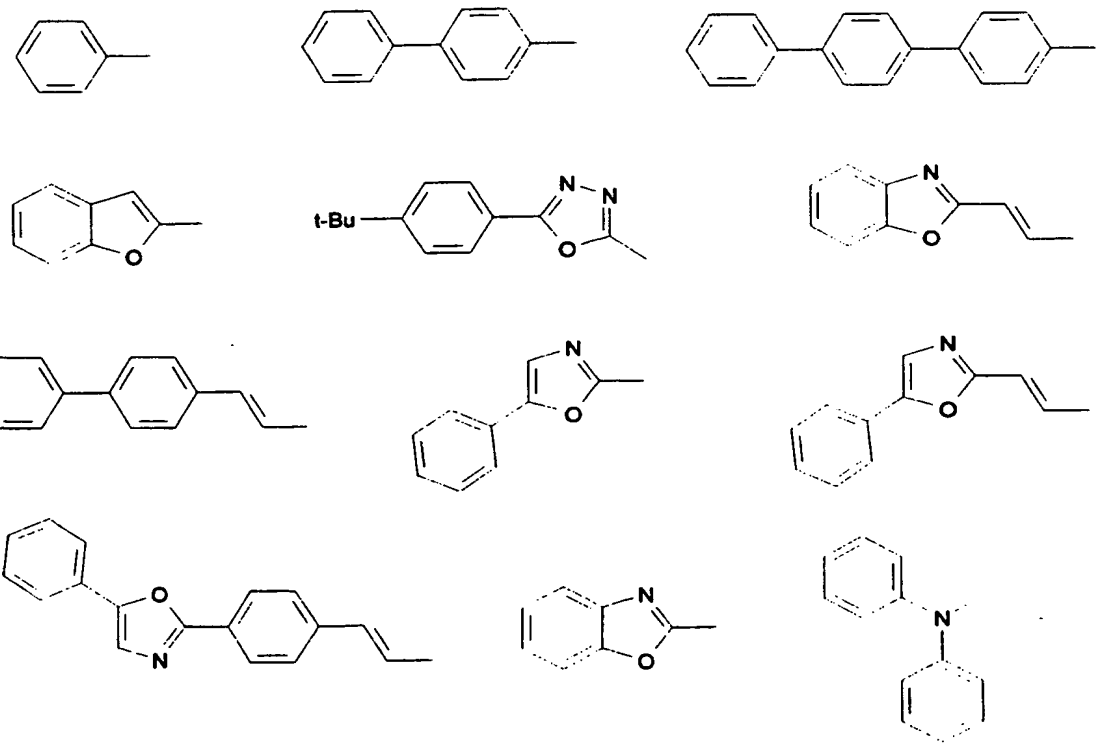
IIId) K^a = M and is selected from the group consisting of:



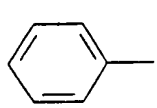
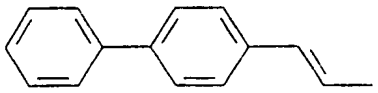
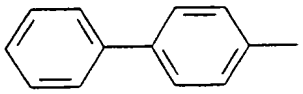
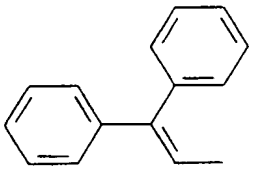
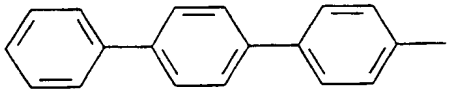
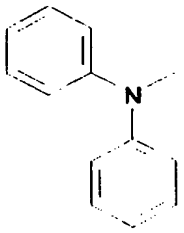
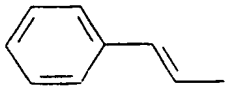
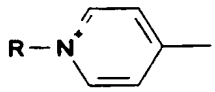
and N^a = L and is selected from the group consisting of:



IIIe) K^a = L = H and M = N^a and is selected from the group consisting of:

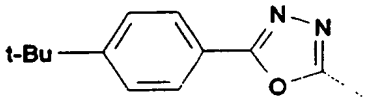
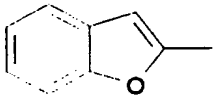
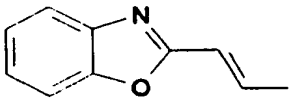
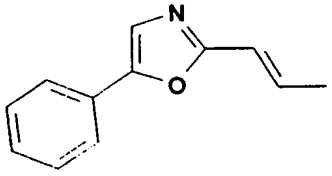
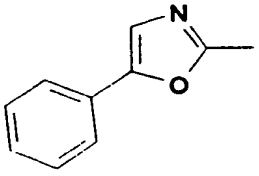
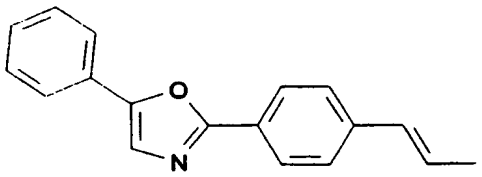
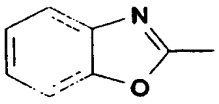


IIIf) K^a = L and is selected form the group consisting of:

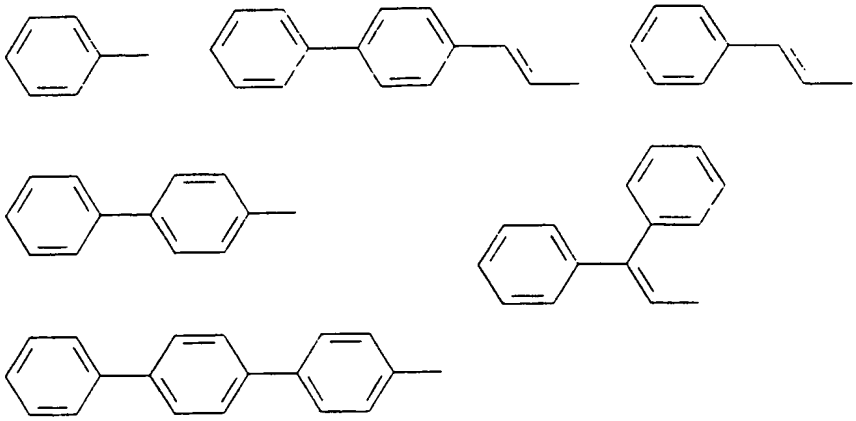









R = Alkyl, $C_2H_4SO_3^-$

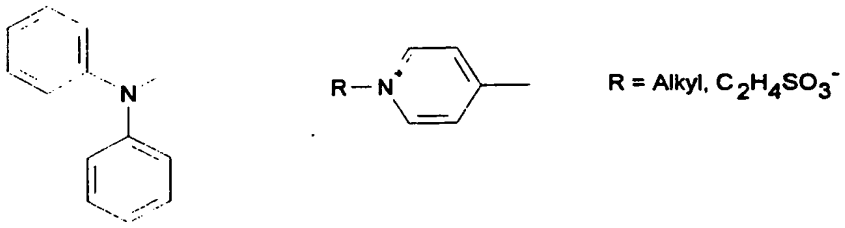
and M = N^a and is selected from the group consisting of:

IIIg) K^a = L and is selected from the group consisting of:



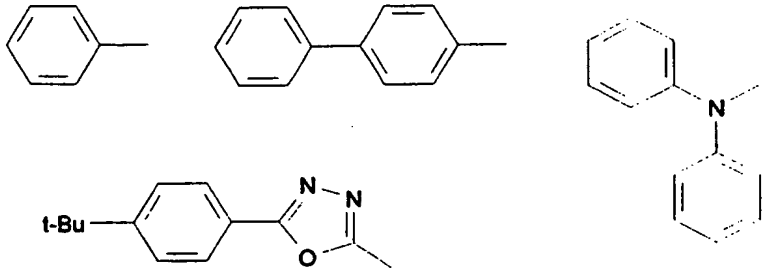
and M = N^a and is selected from the group consisting of:



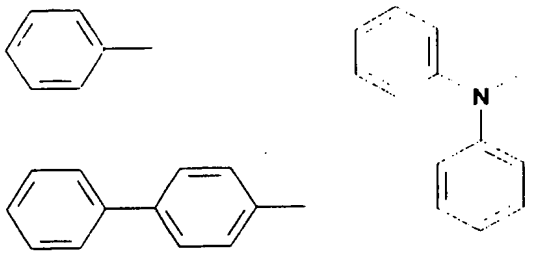
Particularly preferred compounds of the formula (III) are those of the formulae (IIIaa) to (IIIdb):

(IIIaa) K^a = L = M = N^a and is selected from the group consisting of:

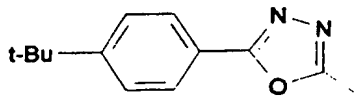
(IIIba) K^a = M = H and N^a = L and is selected from the group consisting of:



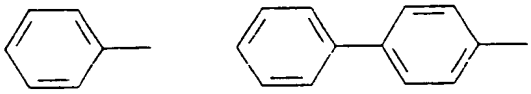
(IIIca) K^a = M and is selected from the group consisting of:



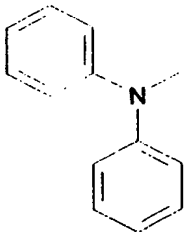
and N^a = L and is:



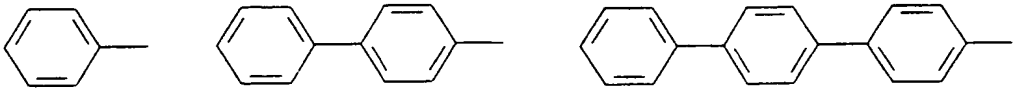
(IIIda) K^a = M and is selected from the group consisting of:



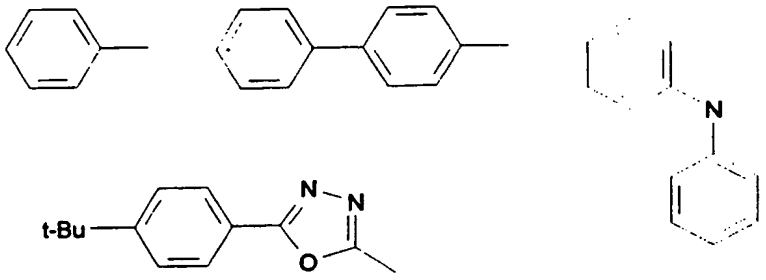
and N^a = L and is:



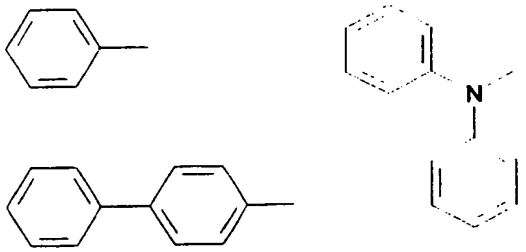
(IIIab) K^a = L = M = N^a and is selected from the group consisting of:



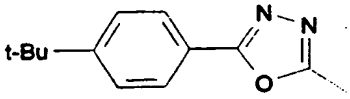
(IIIbb) K^a = L = H and M = N^a and is selected from the group consisting of:



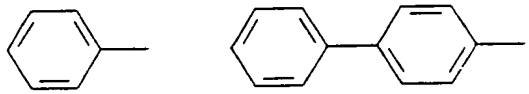
(IIIcb) K^a = L and is selected from the group consisting of:



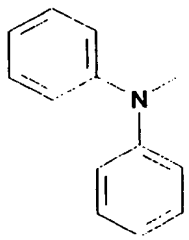
and M = N^a and is:



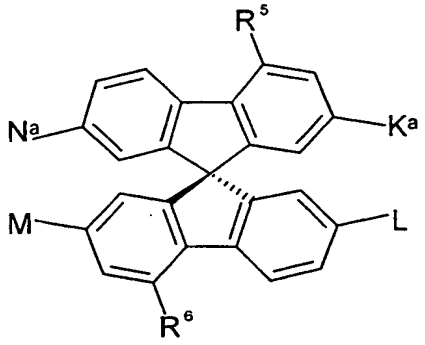
(IIIdb) K^a = L and is selected from the group consisting of:



and M = N^a and is:



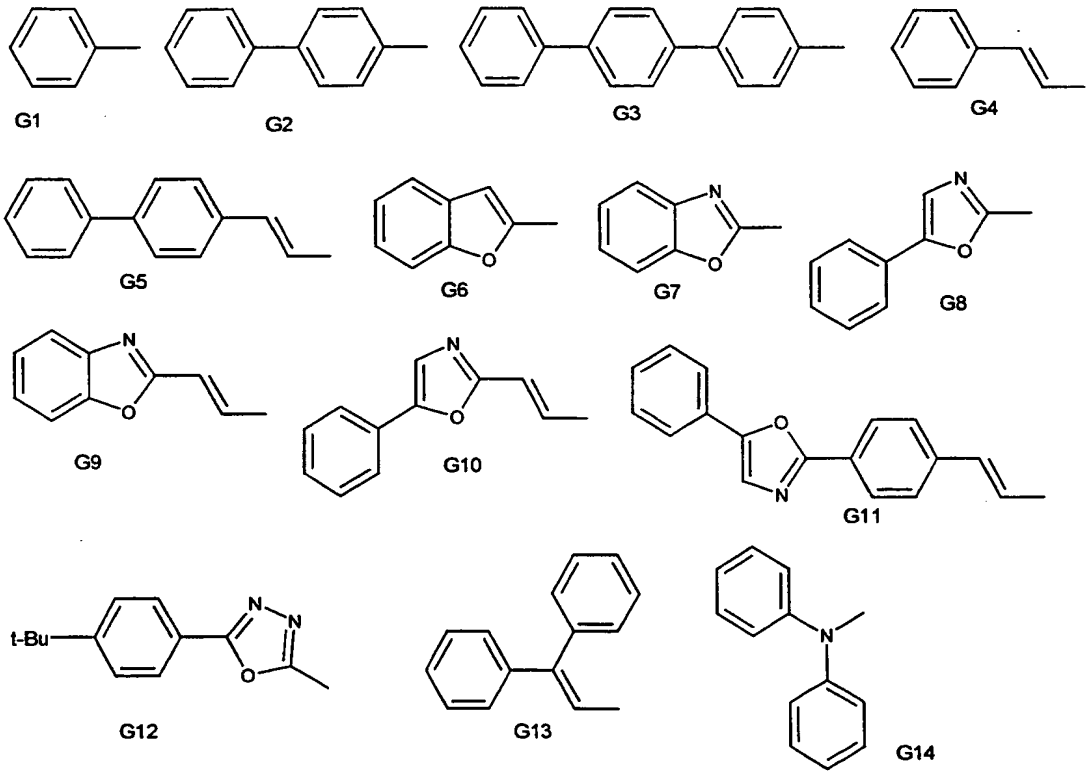
Very particularly preferred spiro compounds are those of the formula (IV)



(IV)

where the symbols have the following meanings:

K^a, L, M, N^a, R^5, R^6, are identical of different and are one of the groups G1 to G14:



and R^5, R^6 can also be identical or different and be hydrogen or a linear of branched alkyl, alkyloxy or ester group having from 1 to 22 carbon atoms, -CN or -NO^2.

Also particularly preferred are spiro-spiro-compounds as disclosed in German patent application „Spiroverbindungen und deren Verwendung„ of February 4, 1998 (applicant Hoechst Research & Technology Deutschland GmbH & Co. KG) which is hereby incorporated by reference.

The spiro compounds used according to the invention are prepared by methods which are known per se in the literature, as are described in standard works on organic synthesis, e.g. Houben-Weyl, Methoden der Organischen Chemie [methods of organic chemistry], Georg-Thieme-Verlag, Stuttgart and in the appropriate volumes of the series „The Chemistry of Heterocyclic Compounds„ by A. Weissberger and E.C. Taylor (editors).

The preparation is here carried out under reaction conditions which are known and suitable for said reactions. Use can also be made of variants which are known per se and are not mentioned in more detail here.

Compounds of the formula (III) are obtained, for example, starting form 9,9'-spirobifluorene whose synthesis is described, for example, by R.G. Clarkson, M. Gomberg, J. Am. Chem. Soc. 52 (1930) 2881.

The compounds of the formula (IIIa) can be prepared, for example, starting with a tetrahalogenation of the 9,9'-spirobifluorene in the 2,2',7,7' positions an a subsequent substitution reaction (see, for example, US 5,026,894) or via a tetraacetylation of the 9,9'-spirobifluorene in the 2,2',7,7' positions with subsequent C-C linkage after conversion of the acetyl groups into aldehyde groups or heterocycle formation after conversion of the acetyl groups into carboxylic acid groups.

The compounds of the formula (IIIb) can be prepared, for example, by a similar method to those of the formula IIIa, with the stoichiometric ratios in the reaction being selected in such a way that the 2,2' or 7,7' positions are functionalized (see, for example, J. H. Weisburger, E. K. Weisburger, F. E. Ray, J. Am. Chem. Soc. 72 (1959) 4253; F. K. Sutcliffe, H. M. Shahidi, D. Paterson, J. Soc. Dyers Colour 94 (1978) 306 and G. Haas, V. Prelog, Helv. Chim. Acta 52 (1069) 1202).

The compounds of the formula (IIIc) can be prepared, for example, by dibromination in the 2,2' positions and subsequent diacetylation in the 7,7' positions of the 9,9'-spirobifluorene and subsequent reaction by a similar method to that for the compounds IIIa.

Compounds of the formulae (IIIe) - (IIIg) can be prepared, for example, by selection of suitably substituted starting compounds in the buildup of the spirobifluorene, e.g. 2,7-dibromospirobifluorene can be built up from 2,7-dibromofluorenone and 2,7-dicarbethoxy-9,9-spirobifluorene by use of 2,7-dicarbethoxyfluorenone. The free 2',7' positions of the spirobifluorene can then be independently further substituted.

For the synthesis of the groups K^a, L, M, N^a, reference may be made, for example, to DE-A 23 44 732, 24 50 088, 24 29 093, 25 02 904, 26 36 684, 27 01 591 and 27 52 975 for compounds having 1,4-phenylene groups; DE-A 26 41 724 for compounds having pyrimidine-2,5-diyl groups; DE-A 40 26 223 and EP-A 0 391 203 for compounds having pyridine-2,5-diyl groups; DE-A 32 31 462 for compounds having pyridazine-3,6-diyl groups; N. Miyaura, T. Yanagi and A. Suzuki in Synthetic Communications 11 (1981) 513 to 519, De-A 3,930,663, M. J. Sharp, W. Cheng, V. Snieckus in Tetrahedron Letters 28 (1987), 5093; G. W. Gray in J. Chem. Soc. Perkin Trans II (1989) 2041 and Mol. Cryst. Liq. Cryst. 172 (1989) 165, Mol. Cryst. Liq. Cryst. 204 (1991) 43 and 91; EP-A 0,449,015; WO 89/12039; WO 89/03821; EP-A 0,354,434 for the direct linking of aromatics and heteroaromatics.

The preparation of disubstituted pyridines, disubstituted pyrazines, disubstituted pyrimidines and disubstituted pyridazines is given, for example, in the appropriate

volumes of the series „The Chemistry of Heterocyclic Compounds„ by A. Weissberger and E. C. Taylor (editors).

The excitation of the above described active narrow band width emitting material can be achieved by optical excitation with an intense light source like a laser (or a flash light) as described and demonstrated in the examples included.

The excitation can also be achieved by electrically pumping in an organic light emitting diode thereby using a special device structure.

A second item of this patent is therefore an electrically pumped device structure for an organic light emitting diode, using the above mentioned emitting materials. An organic laser device of the invention comprises, in order, a substrate, a bottom electrode layer, an organic layer structure comprising at least one spiro compound of the formula I, and a top electrode layer within a laser cavity.

Substrate is made from glass, quartz glass, ceramic, a polymer, such as polyimide, polyester, polyethylene terephthalate, polycarbonate, polyethylene, polyvinyl chloride, or a single crystal semiconductor selected from the group consisting of either undoped, lightly doped, or heavily doped Si, Ge, GaAs, GaP, GaN, GaSb, InAs, InP, InSb, and $Al_xGa_{1-x}As$ where x is from 0 to 1.

The organic laser device can be viewed as a diode which is forward biased when the anode is at a higher potential than the cathode. Under these conditions, bottom electrode layer acts as an anode for hole (positive charge carrier) injection when this bottom electrode is preferably made from a high work function material selected, e.g., from nickel, gold, platinum, palladium, selenium, iridium or an alloy of any combination thereof, tin oxide, indium tin oxide (ITO) or copper iodide, also, an electroconductive polymer such as poly (3-methylthiophene), polyphenylene sulfide or polyaniline (PANI) or poly-3,4-ethylene dioxythiophene (PEDOT). These materials can be used independently or by layering two or more materials such as by film coating PANI or PEDOT on ITO.

On the other hand, top electrode layer can act as a cathode for electron injection when this top electrode is made from a low work function material, preferably a metal or metal alloy, especially selected from, e.g., lithium, aluminum, beryllium, magnesium, calcium, strontium, barium, lanthanum, hafnium, indium, bismuthium, cer, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium or an alloy of any combination thereof or an alloy of one of this metals with another metal.

The laser cavity provides a feedback mechanism to allow one frequency mode for resonance and it is made by external grating, or distributed feedback, or distributed Bragg reflector.

Examples

A. Starting compounds

a) Synthesis of 9,9'-spirobifluorene

6.3 g of magnesium turnings and 50 mg of anthracene are initially placed in 120 ml of dry diethyl ether under argon in a 1 l three-necked flask fitted with reflux condenser and the magnesium is activated for 15 minutes using ultrasound.

62 g of 2-bromobiphenyl are dissolved in 60 ml of dry diethyl ether. About 10 ml of this solution are added to the initially charged magnesium to initiate the Grignard reaction.

After the reaction starts, the 2-bromobiphynyl solution is added dropwise with a further ultrasound treatment in such a way that the solution gently boils under reflux. After the addition is complete, the reaction mixture is boiled under reflux for a further hour with ultrasound.

48.8 g of 9-fluorenone are dissolved in 400 ml of dry diethyl ether and, with further ultrasound treatment, are added dropwise to the Grignard solution. After the addition is complete, the mixture is boiled for a further 2 hours. The

yellow magnesium complex of 9-(2-biphenyl)-9-fluorenol precipitated after cooling the reaction mixture is filtered off with suction and washed with a little ether. The magnesium complex is hydrolyzed in 800 ml of ice water containing 40 g of ammonium chloride. After stirring for 60 minutes, the 9-(2-biphenyl)-9-fluorenol formed is filtered off with suction, washed with water and sucked dry.

The dried 8-(2-biphenyl)-9-fluorenol is the dissolved in 500 ml of hot glacial acetic acid. 0.5 ml of concentrated hydrochloric acid is added to this solution. The solution is allowed to boil for a few minutes and the 9,9'-spirobifluorene formed is precipitated from the hot solution using water (water added until the solution starts to become turbid). After cooling, the product is filtered off with suction and washed with water. The dried product is further purified by recrystallization from ethanol. This gives 66 g (80 %, based on 2-bromobiphenyl) of 9,9'-spirobifluorene as colorless crystals, m.p. 198°C.

b) 2,2'-Dibromo-9,9'-spirobifluorene
(F. K. Sutcliffe, H. M. Shahidi, D. Patterson, J. Soc. Dyers Colour 94 (1978) 306)

3.26 g (10.3 mmol) of 9,9'-spirobifluorene are dissolved in 30 ml of methylene chloride and admixed with 5 mg of $FeCl_3$ (anhydrous) as catalyst. The reaction flask is protected from light. 1.12 ml (21.8 mmol) of bromine in 5 ml of methylene chloride are added dropwise over a period of 30 minutes while stirring. After 24 hours, the resulting brown solution is washed with saturated aqueous $NaHCO_3$ solution and water to remove excess bromine. The organic phase is, after drying over Na_2SO_4, evaporated on a rotary evaporator. The white residue is recrystallized from methanol, giving 3.45 g (70 %) of the dibromo compound as colorless crystals, m.p. 240°C.

c) 2,2',7,7'-Tetrabromo-9,9'-spirobifluorene

80 mg (0.5 mmol) of anhydrous $FeCl_3$ are added to a solution of 3.16 g (10.0 mmol) of 9,9'-spriobifluorene in 30 ml of methylene chloride, and 2.1 ml (41 mmol) of bromine in 5 ml of methylene chloride are added dropwise over a period of 10 minutes. The solution is refluxed for 6 hours. On cooling, the product precipitates. The precipitate is filtered off with suction and washed with a little cold methylene chloride. After drying, 6.0 g (95 %) of the tetrabromo compound are obtained as a white solid.

d) 2-Bromo-9,9'-spirobifluorene and 2,2'7-tribromo-9,9'-spirobifluorene can be prepared in a similar manner using different stoichiometry.

e) 9,9'-Spirobifluorene -2,2'-dicarboxylic acid from 2,2'-dibromo-9,9'-spirobifluorene via 2,2'-dicyano-9,9'-spirobifluorene

1.19 g of 2,2'-dibromo-9,9'-spirobifluorene and 0.54 g of CuCN are heated under reflux in 5 ml of DMF for 6 hours. The brown mixture obtained is poured into a mixture of 3 g of $FeCl_3$ (hydrated) and 1.5 ml of concentrated hydrochloric acid in 20 ml of water. The mixture is maintained at from 60 to 70°C for 30 minutes, to destroy the Cu complex. The hot aqueous solution is extracted twice with toluene. The organic phases are then washed with dilute hydrochloric acid, water and 10 % strength aqueous NaOH. The organic phase is filtered and evaporated. The yellow residue obtained is recrystallized from methanol. This gives 0.72 g (80 %) of 2,2'-dicyano-9,9'-spirobifluorene as pale yellow crystals (melting range from 215 to 245°C).

3 g of 2,2'-dicyano-9,9'-spirobifluorene are heated under reflux with 25 ml of 30 % strength aqueous NaOH and 30 ml of ethanol for 6 hours. The disodium salt of the spirobifluorenedicarboxylic acid is precipitated as a yellow solid which is filtered of and heated in 25 % strength aqueous HCl to obtain the free acid. The spirobifluorene dicarboxylic acid is recrystallized form glacial

acetic acid. This gives 2.2 g (66.6 %) of white crystals (m.p. 376°C, IR bands 1685 cm^{-1} C=O).

9,9'-Spirobifluorene-2,2',7,7'-tetracarboxylic acid can be prepared in a similar manner form 2,2',7,7'-tetrabromo-9,9'-spirobifluorene.

f) 9,9'-Spirobifluorene-2,2'-dicarbonxylic Acid from 9,9'-spirobifluorene via 2,2'-diacetyl-9,9'-spirobifluorene
(G. Haas, V. Prelog, Helv. Chim. Acta 52 (1969) 1202; V. Prelog, D. Bedekovic, Helv. Chim. Acta 62 (1979) 2285)

A solution of 3.17 g of 9,9'-spirobifluorene in 30 ml of absolute carbon disulfide is, after addition of 9.0 g of finely powdered, anhydrous $AlCl_3$, admixed dropwise over a period of 10 minutes while stirring with 1.58 g of acetyl chloride in 5 ml of absolute carbon disulfide and is boiled under reflux for 1 hour. The mixture is evaporated to dryness under reduced pressure and is admixed at 0°C with 100 g of ice and 50 ml of 2N hydrochloric acid. After a conventional workup, the crude product is separated chromatographically over silica gel using benzene/ethyl acetate (10:1). This gives 3.62 g (89 %) of 2,2'-diacetyl-9,9'-spirobifluorene (recrystallized from chloroform/ethyl acetate, m.p. from 255 to 257°C) and 204 mg of 2-acetyl-9,9'-spirobifluorene (recrystallized from chloroform/benzene, m.p. 225°C). [In addition, the chromatography also enables the 2,2',7-triacetyl-9,9'-spirobifluorene (m.p. from 258 to 260°C) and 2,2',7,7'-tetraacetyl-9,9'-spirobifluorene (m.p. >300°C) to be isolated, recrystallized from ethyl acetate/hexane].
2,2',7-Triacetyl- and 2,2',7,7'-tetraacetyl-9,9'-spirobifluorene can be obtained as main product using a different stoichiometry.
First 7.2 g of bromine and then a solution of 3.0 g of 2,2'-diacetyl-9,9'-spirobifluorene in a little dioxane are added dropwise at 0°C while stirring to a solution of 6.0 g of sodium hydroxide in 30 ml of water. After stirring for a further hour at room temperature, the clear yellow solution is admixed with 1 g of sodium hydrogen sulfite dissolved in 20 ml of water. After acidification with

concentrated hydrochloric acid, the precipitated colorless product is filtered off and washed with a little water. Recrystallization with ethanol gives 9,9'-spirobifluorne-2,2'-dicarboxylic acid as clear prisms (m.p. 352°C).

9,9'-Spirobifluorene-2-carboxylic acid, 9,9'-spirobifluorene-2,2',7'-tricarboxylic acid and 9,9'-spirobifluorene-2,2',7,7'-tetracarboxylic acid can be prepared in a similar manner.

g) 2,2'-Bis(bromomethyl)-9,9'-spirobifluorene from 2,2'-dicarboxy-9,9'-spirobifluorene via 9,9'-spirobifluorene-2,2'-dimethanol
(V. Prelog, D. Bedekovic, Helv. Chim. Acta 62 (1979) 2285)

At room temperature, 10 g of a 70% strength by weight solution of sodium dihydrobis(2-methoxyethoxy)aluminate (Fluka) in benzene are slowly added dropwise to a suspension of 2.0 g of 2,2'-dicarboxy-9,9'-spirobifluorene (free carboxylic acid) in 20 ml of benzene. After boiling for 2 hours under reflux, during which time the carboxylic acid dissolves, the excess reducing agent is decomposed at 10°C using water, the mixture is acidified with concentrated hydrochloric acid and is extracted by shaking with chloroform.

After washing with water and drying over magnesium sulfate, the organic phase is evaporated and the residue is recrystallized from benzene. This gives 1.57 g of 9,9'-spirobifluorene-2,2'-dimethanol (m.p. from 254 to 255°C). 91.5 g of a 33 % strength aqueous solution of hydrogen bromide in glacial acetic acid are added dropwise to a solution of 13.5 g of 9,9'-spirobifluorene-2,2'-dimethanol in 400 ml of benzene and the mixture is boiled under reflux for 7 hours. The mixture is then admixed with 200 ml of water and the organic phase is washed with water, dried over magnesium sulfate and evaporated. Chromatography over silica gel using benzene gives 11.7 g 2,2'-bis(bromomethyl)-9,9'-spirobifluorene as colorless platelets (m.p. from 175 to 177°C).

h) A solution of 380 mg of 9,9'-spirobifluorene-2,2'-dimethanol in 15 ml of toluene is admixed with 5 g of chromium(VI) oxide on graphite (Seloxcette, Alpha Inorganics) and the mixture is refluxed for 48 hours under nitrogen. It is then filtered with suction through a glass filter and the filtrate is evaporated. Chromatography over silica gel using chloroform and crystallization from methylene chloride/ether gives 152 mg of 9,9'-spirobifluorene-2,2'-dicarbaldehyde (m.p. >300°C) and 204 mg of 2'-hydroxymethyl-9,9'-spirobifluorene-2-carbaldehyde (m.p. from 262 to 263°C).

i) 2,2'-Diamino-9,9'-spirobifluorene

A mixture of 150 ml of concentrated aqueous HNO_3 and 150 ml of glacial acetic acid are added dropwise to a boiling solution of 15.1 g of 9,9'-spirobifluorene in 500 ml of glacial acetic acid over a period of 30 minutes and the solution is subsequently refluxed for a further 75 minutes. After cooling and allowing the solution to stand for 1 hour, the same volume of water is added and the product is thereby precipitated. After filtration with suction, 18.5 g of yellow crystals (m.p. from 220 to 224°C) of 2,2'-dinitro-9,9'-spirobifluorene are obtained. Recrystallization from 250 ml of glacial acetic acid gives 12.7 g of pale yellow crystalline needles (m.p. from 245 to 249°C, analyrtically pure from 249 to 250°C).

A mixture of 4.0 of dinitrospirobifluorene and 4.0 of iron powder are heated under reflux in 100 ml of ethanol, while 15 ml of concentrated HCl are added dropwise over a period of 30 minutes. After refluxing for a further 30 minutes, excess iron is filtered off. The green filtrate is added to a solution of 400 ml of water, 15 ml of concentrated NH_4OH and 20 g of sodium potassium tartrate. The white diamine is filtered off from the dark green solution of the iron complex. To purify the diamine, it is dissolved in dilute HCl and stirred at room temperature with activated carbon (Darco) and filtered off. The filtered solution is neutralized dropwise with NH_4OH while stirring (precision glass stirrer) and the precipitated product is filtered off with suction. This gives 3.5 g of white 2,2'-diamino-9,9'-spirobifluorene which can be recrystallized from

ethanol (m.p. 243°C).

j) Synthesis of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene by bromination of solid 9,9'-spirobifluorene using bromine vapor.

3.16 g (10 mmol) of finely powdered 9,9'-spirobifluorene are placed in a flat porcelain evaporating dish (∅ 2 about15 cm). This dish is placed in a desiccator (∅ about 30 cm), on the perforated intermediate plate. On the bottom of the desiccator there are 15.6 g (4.8 ml, 96 mmol) of bromine in a crystallizing dish. The desiccator is closed, but with the ventilation tap opened so that the HBr formed can escape. The desiccator is placed overnight in the fume hood. On the next day, the porcelain dish containing the product, which has been colored orange by bromine, is taken from the desiccator and left to stand in the fume hood for at least a further 4 hours so that excess bromine and HBr can escape.
The product is dissolved in 150 ml of dichloromethane and washed until colorless with 50 ml each of sodium sulfite solution (saturated), sodium hydrogen carbonate solution (saturated) and water. The dichloromethane solution is dried over sodium sulfate and evaporated on a rotary evaporator. The residue is purified by recrystallization from dichloromethane/pentane 4:1. Yield: 5.7 (92 %) of colorless crystals.
^{1}H-NMR ($CDCl_3$, ppm): 6.83 (d, J = 1.83 Hz, 4 H, H-1,1', 8,8'); 7.54 (dd; J = 7.93, 1.83 Hz, 4 H, H-3,3',6,6'); 7.68 (d, J = 7.93 Hz, 4H, H-4,4',5,5').

k) Synthesis from 2,2',4,4',7,7'-hexabromo-9,9'-spirobifluorene

200 mg of anhydrous $FeCl_3$ are added to a solution of 3.16 g (10 mmol) of 9,9'-spirobifluorene in 20 ml of methylene chloride and the mixture is treated with ultrasound. The reaction flask is protected from light by means of aluminum foil. Subsequently, at the boiling point, 9.85 g (3.15 ml, 62 mmol) of bromine in 5 ml of methylene chloride are added dropwise over a period of 15 minutes. The solution is boiled under reflux and treated with ultrasound for a

further 20 hours. After cooling, petroleum ether is added and the mixture is filtered with suction. The product is further purified by recrystallization from THF/methanol and drying for 5 hours at 80°C. Yield: 6.15 g (77 %) of colorless crystals.

^{1}H-NMR ($CDCl_3$, ppm): 6.76 (d, J = 1.53 Hz, 2H, H 1,1'); 6.84 (d, J = 1.83 Hz, 2H, H-8,8'); 7.60 (dd, J = 8.54, 1.83 Hz, 2H, H-6,6'); 7.75 (d, J= 1.53 Hz, 2H, H-3,3'); 8.49 (d, J = 8.54 Hz, 2 H, H-5m5').

l) Synthesis of 2,7-dibromo-9,9'-spirobifluorene

The Grignard reagent prepared from 0.72 g (30 mmol of magnesium turnings and 5.1 ml (30 mmol) of 2-bromobiphenyl in 15 ml of diethyl ether is added dropwise over a period of 2 hours, while stirring (in an ultrasonic bath), to a boiling suspension of 10.0 g (29.6 mmol) of 2,7 dibromo-9-fluorenone in 100 ml of dry diethyl ether. After the addition is complete, the mixture is boiled for a further 3 hours. After cooling overnight, the precipitated solid is filtered off with suction and washed with cold ether. The magnesium complex filtered off is hydrolyzed in a solution of 15 g of ammonium chloride in 250 ml of ice water. After 1 hour, the 9-(2-biphenylyl)-2,7-dibromo-9-fluorenol formed is filtered off with suction, washed with water and sucked dry. For the ring-closure reaction, the dried fluorenol is boiled in 100 ml of glacial acetic acid for 6 hours, after addition of 3 drops of concentrated HCl. The mixture is allowed to crystallize overnight, the product formed is filtered off with suction and is washed with glacial acetic acid and water.

Yield: 11 g (77 %) of 2,7-dibromo-9,9'-spirobifluorene. It can be further purified by recrystallization from THF.

^{1}H-NMR ($CDCl_3$, ppm): 6.73 (sd, J = 7.63 Hz, 2 H, H-1',8'); 6.84 (d, J = 1.83 Hz, 2 H, H-1,8); 7.15 (td, J = 7.63, 1.22 Hz, 2 H, h-2',7'); 7.41 (td, J = 7.63, 1.22 Hz, 2H, H-3',6'); 7.48 (dd, J = 8.24, 1.83 Hz, 2H, H-3,6); 7.67 (d, J = 8.24 Hz; 2 H; H-4,5); 7.85 (d, J= 7.63, 2H, H-4',5').

m) Synthesis of 2,7-dicarbethoxy-9,9'-spirobifluorene

The Grignard reagent prepared from 0.97 g (40 mmol) of magnesium turnings and 9.32 g (6.8 ml, 40 mmol) of 2-bromobiphenyl) in 50 ml of dry diethyl ether is added dropwise over a period of 2 hours to a boiling solution of 13 g (40 mmol) of 2,7 dicarbethoxy-9-fluorenone in 100 ml of dry diethyl ether. After the addition is complete, the mixture is boiled for a further 3 hours. After cooling overnight, the precipitated solid is filtered off with suction and washed with cold ether. The magnesium complex filtered off with suction is hydrolyzed in a solution of 15 g of ammonium chloride in 250 ml of ice water. After 1 hour, the 9-(2-biphenyl)-2,7-dicarbethoxy-9-fluorenol formed is filtered off with suction, washed with water and sucked dry. For the ring closure reaction, the dried fluorenol is boiled in 100 ml of glacial acetic acid fro 6 hours, after addition of 3 drops of concentrated HCl. The mixture is allowed to crystallize overnight, the product formed is filtered off with suction and washed with glacial acetic acid and water.

Yield: 15.1 g (82 %) of 2,7-dicarbethoxy-9,9'-spirobifluorene. It can be further purified by recrystallization from ethanol.

^{1}H-NMR ($CDCl_3$, ppm): 1.30 (t, J = 7.12 Hz, 5 H, ester-CH_3); 4.27 (q, J= 7.12 Hz, 4H, ester-CH_2); 6.68 (d, J = 7.63 Hz, 2H, H-1',8'); 7.11 (td, J = 7.48, 1.22 Hz, 2H, H-2',7'); 7.40 (td, J = 7.48, 1.22 Hz, 4H, H-1,8,3',6'); 7.89 (dt, J = 7.63, 0.92 Hz, 2H, H-4',5'); 7.94 (dd, J = 7.93, 0.6 Hz, 2H, H-4,5); 8.12 (dd, J = 7.93, 1.53 Hz, 2 H, H-3,6).

n) Synthesis of 2,7-dibromo-2',7'-diiodo-9,9'-spirobifluorene

In a 250 ml of three-necked flask fitted with reflux condenser and dropping funnel, a suspension of 2.37 g of 2,7 dibromo-9,9'-spirobifluorene in 50 ml of glaciyl acetic acid is admixed at 80°C with 5 ml of water and, after addition of 2 ml of concentrated sulfurid acid, 1.27 g of iodine, 0.53 iodic acid and 5 ml of carbon tetrachloride, is stirred until the iodine color disappears. The solid is subsequently filtered off with suction and washed well with water. After drying,

the precipitate is dissolved in 150 ml of dichloromethane and washed successively with Na_2SO_3 solution, $NaHCO_3$ solution and water. The dichloromethane phase is dried over Na_2SO_4 and subsequently evaporated. This gives colorless crystals of 2,7 dibromo-2',7'-diiodo-9,9'-spirobifluorene in quantitative yield. It can be further purified by recrystallization from dichloromethane/pentane.

6.80 (d, J = 1.83 Hz, 2H), 6.99 (d, J = 1.53 Hz, 2H), 7.51 (dd, J = 8.24, 1.83 Hz, 2H), 7.54 (d, J = 7.93 Hz, 2H), 7.65 (d, J = 8.24 Hz, 2H), 7.72 (dd, J = 8.24, 1.53 Hz, 2H).

B Synthesis examples

Example 1

2,2'-Bis(benzofuran-2-yl)-9,9'-spirobifluorene (using a method similar to that of W. Sahm, E. Schinzel, P. Jürges, Liebigs Ann. Chem. (1974) 523)

2.7 g (22 mmol) of salicylaldehyde and 5.0 g (10 mmol) of 2,2'-bis(bromomethyl)-9,9'-spirobifluorene are dissolved at room temperature in 15 ml of DMF and admixed with 0.9 g (22.5 mmol) of pulverized NaOH and a spatula tip of KI. The miture is heated to boiling and stirred for 1 hour at the boiling point. After cooling, the reaction solution is admixed with a mixture of 0.5 ml of concentrated hydrochloric acid, 7 ml of water and 7 ml of methanol. The mixture is stirred for a further 1 hour at room temperature, the crystalline reaction products are filtered off with suction, washed with cold methanol, then with water and dried in vacuo at 60°C. This gives 4.6 g (79 %) 2,2'-bis(2-formylphenyloxymethyl)-9,9-spirobifluorene.

5.85 g (10 mmol) 2,2'-bis(2-formylphenyloxymethyl)-9,9'-spirobifluorene are mixed in 10 ml of toluene with 2.1 g (22.5 mmol) of freshly distilled aniline. A spatula tip of p-toluenesulfonic acid is added and the mixture is heated at the boiling point (from about 3 to 5 hours). On cooling the reaction mixture, the corresponding bis-benzylidene-phenylamine precipitate in crystalline form. It is filtered off with suction,

washed with methanol and dried in vacuo at 60°C. It can be further purified by recrystallization from DMF.

7.35 g (10 mmol) of the bis-benzylidenephenylamine and 0.62 g (11 mmol) of KOH are introduced under nitrogen into 30 ml of DMF. The mixture is subsequently heated at 100°C for 4 hours while stirring. After cooling to room temperature, the precipitate is filtered off with suction and washed with a little DMF and water. After drying at 60°C in a vacuum drying oven, the 2,2'-bis(benzofuran-2-yl)-9,9'-spirobifluorene can be purified by recrystallization from methyl benzoate.

Example 2

2,2',7,7'-Tetra(benzofuran-2-yl)-9,9'-spirobifluorene can be prepared by a similar method to Example 1 using an appropriately altered stoichiometry.

Example 3

2,2',7,7'-Tetraphenyl-9,9'-spirobifluorene

5 g (7.9 mmol) of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene, 3.86 g (31.6 mmol) of phenylboronic acid, 331.5 mg (1.264 mmol) of triphenylphosphine and 70.9 mg (0.316 mmol) of palladium acetate are slurried in a mixture of 65 ml of toluene and 40 ml of aqueous sodium carbonate solution (2 M). With vigorous stirring, the mixture is boiled under reflux for 24 hours. After cooling to room temperature, the solid is filtered off with suction, washed with water and dried in vacuo at 50°C. 2.58 g are obtained. The filtrate is extracted with 50 ml o toluene and the dried organic phase is evaporated to dryness. This gives a further 1.67 g.

Total yield: 4.25 g (86 %)

Example 4

2,2',7,7'-Tetrakis(biphenyl)-9,9'-spirobifluorene

5 g (7.9 mmol) of 2,2',7,7'-tetrabromospirobifluorene, 6.57 g (33.2 mmol) of biphenylboronic acid, 331.5 mg (1.264 mmol) of triphenylphosphine and 70.9 mg (0.316 mmol) of palladium acetate are slurried in a mixture of 65 ml of toluene and

40 ml of queous sodium carbonate solution (2 M). With vigorous stirring, the mixture is boiled under reflux for 24 hours. After cooling to room temperature, the solid is filtered off with suction, washed with water and dried in vacuo at 50°C.
Yield: 5.95 g (81 %)

Example 5
Synthesis of 2,2',7,7'-tetrabiphenylyl-9,9'-spirobifluorene

In a 250 ml two-necked flask fitted with reflux condenser and precision glass tirrer, 5.5 g of tetrabromospirobifluorene, 7.2 g of biphenylboronic acid and 400 mg of terakis(triphenylphosphine)palladium are slurried in a mixture of 100 ml of toluene and 50 ml of potassium carbonate solution. The mixture is boiled under reflux for 8 hours under a blanket of inert gas while stirring with a precision glass stirrer. After cooling, the product is filtered off with suction, the precipitate is washed with water and dried. The toluene phase is separated off from the filtrate and the aqueous phase is extracted once with chloroform. The combined organic phases are dried over sodium sulfate and evaporated on a rotary evaporator, thus giving a second fraction of the product. The two product fractions are combined (8 g) and dissolved in chloroform. The chloroform solution is boiled with activated carbon and filtered through a short column of silica gel. After evaporation on a rotary evaporator and recrystallization from chloroform/Pentane, colorless crystals which fluoresce blue under UV illumination are obtained. Melting point: 408°C (DSC).
^{1}H-NMR ($CDCl_3$, ppm): 7.14 (d, J = 1.53 Hz, 4H); 7.75 (dd, J = 7.93, 1.53 Hz, 4H); 8.01 (d, J= 7.93 Hz, 4H); 8.01 (d, J = 7.93 Hz, 4H); 7.34 (dd, J = 7.32, 1.37 Hz, 4H); 7.42 (t, J = 7.32 Hz, 8H); 7.58 (24 H).

Example 6
Synthesis of 2,2',4,4',7,7'-hexabiphenylyl-9,9'-spirobifluorene

In a 250 ml two-necked flask fitted with reflux condenser and precision glass stirrer, 1,6 g of hexabromospirobifluorene and 3 g of biphenylboronic acid are slurried in a mixture of 50 ml of toluene and 50 ml of 1 M potassium carbonate solution. The

mixture is refluxed under nitrogen and 115 mg of tetrakis(triphenylphosphine)palladium in 5 ml of toluene are added. The mixture is boiled under reflux for 7 hours while stirring. After the reaction is complete, the cooled solution is filtered and the filtrate is extracted twice by shaking with water (to improve the phase separation, chloroform is added). The organic phase is dried over sodium sulfate, filtered through a short column of silica gel and subsequently evaporated on a rotary evaporator. The product is further purified by recrystallization from dichloromethane/pentane. This gives 2 g (80 %) of colorless crystals which fluoresce blue under UV illumination.

^{13}C-NMR [360 Mhz; ATP, broad-band decoupled] ($CDCl_3$, ppm):
65.94 (1C, spiro-C); 126.95 (6C, CH), 126.97 (6C, CH), 127.17 (6C, CH), 127.35 (6C, CH), 127.36 (6C, CH), 127.39 (6C, CH), 127.52 (6C, CH), 128.73 (6C, CH), 128.75 (6C, CH), 128.94 (6C, CH), 129.90 (4C, CH), 137.77 (2C), 137.86 (2C), 139.43 (2C), 139.69 (2C), 139.89 (2C), 140.09 (2C), 140.17 (2C), 140.22 (2C), 140.30 (2C), 140.63 (2C), 140.64 (2C), 140.68 (2C), 140.72 (2C), 140.74 (2C), 150.45 (2C), 150.92 (2C).

Example 7

Synthesis of 2,2'-bis[5-(p-t-butylphenyl)-1,3,4-oxadiazol-2-yl]-9,9'-spirobifluorene from 9,9'-spirobifluorene-2,2'-dicarboxylic acid chloride and 5-(4-t-butylphenyl)tetrazole

a) Synthesis of 5-(4-t-butylphenyl)tetrazole

In a 250 ml round-bottomed flask fitted with reflux condenser, 4.9 g of p-t-butylbenzonitrile, 3.82 g of lithium chloride and 5.85 g of sodium azide and 8.2 g of triethylammonium bromide in 100 ml of DMF are heated at 120°C for 8 hours. After cooling to room temperature, 100 ml of water are added and the mixture is admicxed in an ice bath with dilute hydrochloric acid until no further solid precipitates. The precipitate is filtered off with suction, washed with water and dried. Recrystallization from ethanol/water gives 4.4 g of colorless crystals.

b) 9,9'-Spirobifluorene-2,2'-dicarboxylic acid chloride

In a 100 ml flask fitted with reflux condenser and drying tube, 2 g (5 mmol) of 9,9'-spirobifluorene-2,2'-dicarboxylic acid together with 20 ml of freshly distilled thionyl chloride and 3 drops of DMF are boilde under reflux for 4 hours. After cooling, the reflux condenser is replaced by a distillation bridge and excess thionyl chloride is distilled off in vacuo, 40 ml of petroleum ether (30 - 60°C) are added to the residue and are distilled off, leaving the crystalline acid chloride.

c) 2,2'-Bis[5-(p-t-butylphenyl)-1,3,4-oxadiazol-2-yl]-9,9'-spirobifluorene

2.0 g (11 mmol) of 5-(4-t-butylphenyl)tetrazole dissolved in 20 ml of anhydrous pyridine are added to the acid chloride and the mixture is refluxed under inert gas for 2 hours. After cooling, the mixture is added into 200 ml of water and allowed to stand for 2 hours. The precipitated oxadiazole derivative is fikltered off with suction, washed with water and dried in vacuo. It is subsequently chromatographed over silica gel using chloroform/ethyl acetate (99:1) and recrystallized from chloroform/pentane. This gives 2.4 g of colorless crystals.

^{1}H-NMR ($CDCl_3$, ppm):

1.31 (s, 18 H, t-butyl), 6.77 (d, J = 7.32 Hz,, 2 H), 7.18 (td, J = 7.48, 1.22 Hz, 2 H), 7.44 (td, J = 7.40, 1.22 Hz, 2 H); 7.46 (d, J = 8.54 Hz, 4 H), 7.50 (d, J = 1.22 Hz, 2 H), 7.94 (d, J = 8.54 Hz, 4 H), 8.02 (d, J = 7.93 Hz, 6 H), 8.20 (dd, J = 7.93 Hz, 1.53 Hz, 2 H).

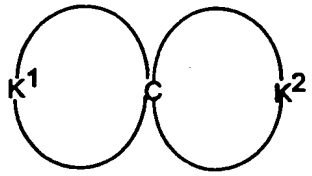
Films of the claimed compounds can be prepared by spin coating of vapor deposition on transparent substrates. In the following examples films have been prepared by spin coating from a chloroform solution with a concentration of 10 mg/ml on a non patterned glass substrate. Smooth transparent films were obtained for example with 2,2´,7,7´-tetraphenyl-9,9´-spirobifluoren (spiro-4PP), 2,2´,7,7´-tetrakis(biphenylyl)-9,9´-spirobifluoren (spiro-6PP), and 2,2´,7,7´-tetrakis(terphenylyl)-9,9´-spirobifluoren (spiro-8PP).

These films are irradiated with UV light supplied from a pulsed nitrogen laser light source, at a wavelength of 337 nm (pulse wide 1-2 ns, repetition rate 20 Hz). The spectrum of the emitted light was recorded with an integration time of about 0.3 s. At low energy density of the exciting UV light, the usual blue photoluminescence spectra of each compound can be observed. By increasing the energy density of the exciting UV light, spectral narrowing in the emitted blue light of the three films can be observed.

The full width at halve height (FWHM) of the emitted blue light collapses down to 2 to 3 nm in the experiments.

Claims:

1. Use of spiro compounds of the formula (I)

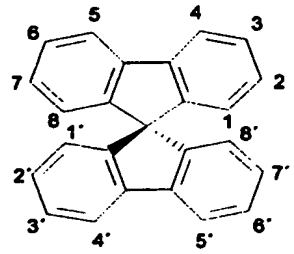


(I)

where

K^1 and K^2 are, independently of one another,conjugated systems, as a laser dye.

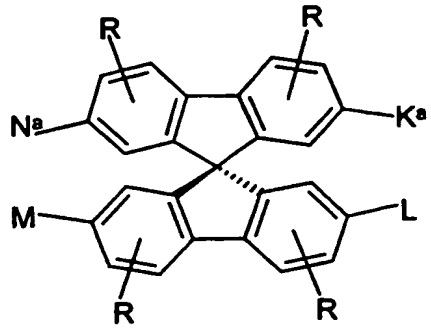
2. Use as claimed in claim 1, wherein the spiro compound used is a spirobifluorene of the formula (II)



(II)

where the benzo groups can be substituted and/or fused independently of one another.

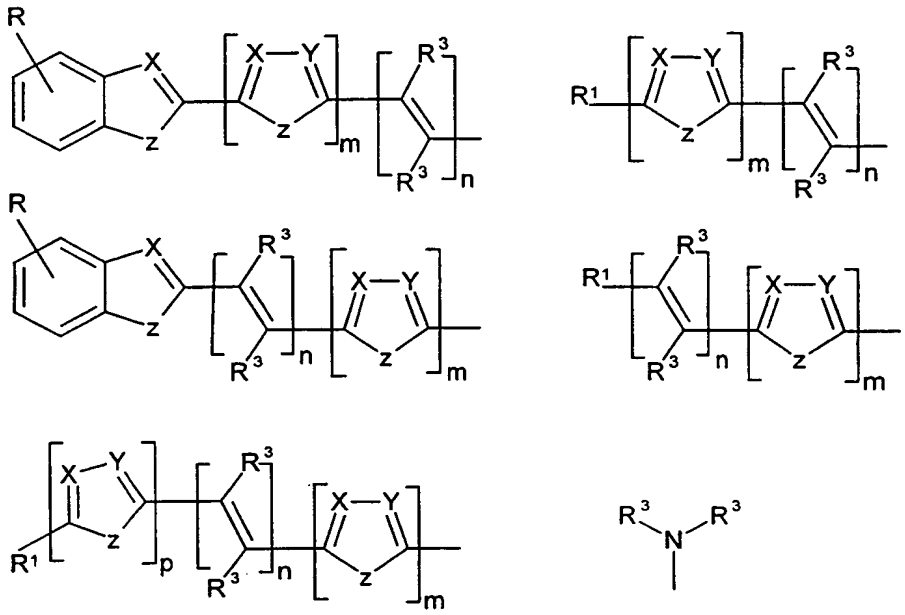
3. Use as claimed in claim 1 and/or 2, wherein use is made of a spirobifluorene derivative of the formula (III)



(III)

where the symbols and indices have the following meaning:

K^a, L, M, N^a are identical or different and are



R can be identical or diferent on each appearance and have the same meanings as K^a, L, M, N^a or is H, a linear or branched alkyl, alkoxy or ester group having from 1 to 22 carbon atoms, -CN, $-NO_2$, $-NR^2R^3$, -Ar or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furyl, with each of these groups being able to bear one or two radicals R,

m, n, p are 0, 1, 2 or 3;

X, Y are identicyl or different and are CR or nitrogen;

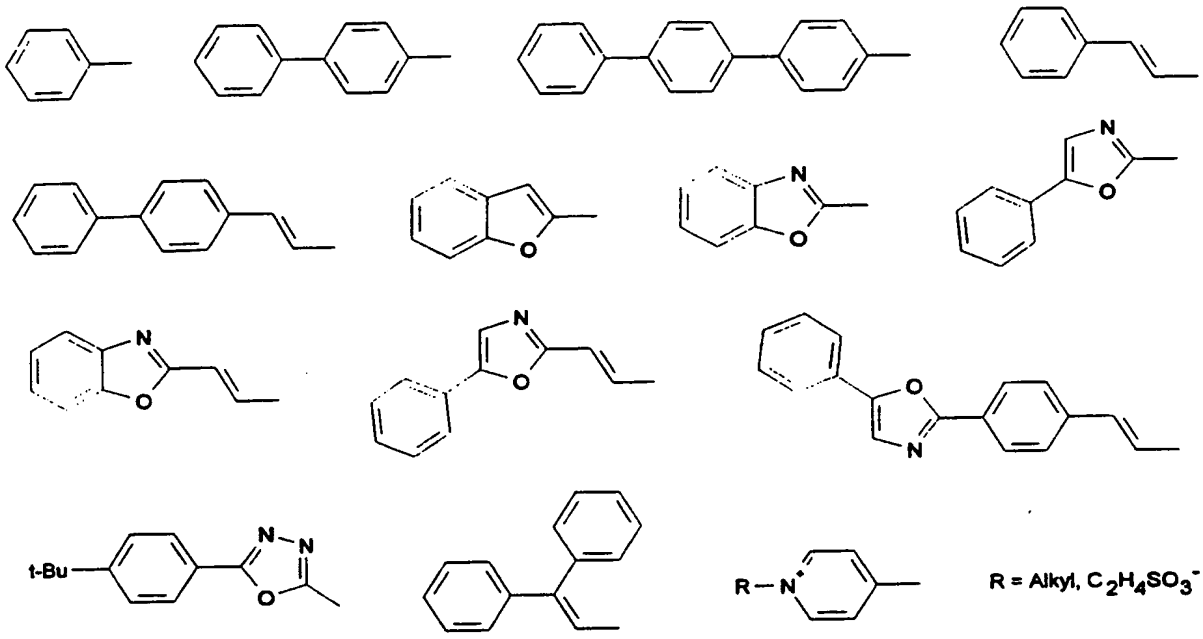
Z is -O-, -S-, $-NR^1$-, $-CR^1R^4$-, -CH=CH-, -CH=N-;

R^1, R^4 can be identical or different and have the same meanings as R;

R^2, R^3 are identical or different and are H, a linear or branched alkyl group having from 1 to 22 carbon atoms, -Ar, 3-methylphenyl.

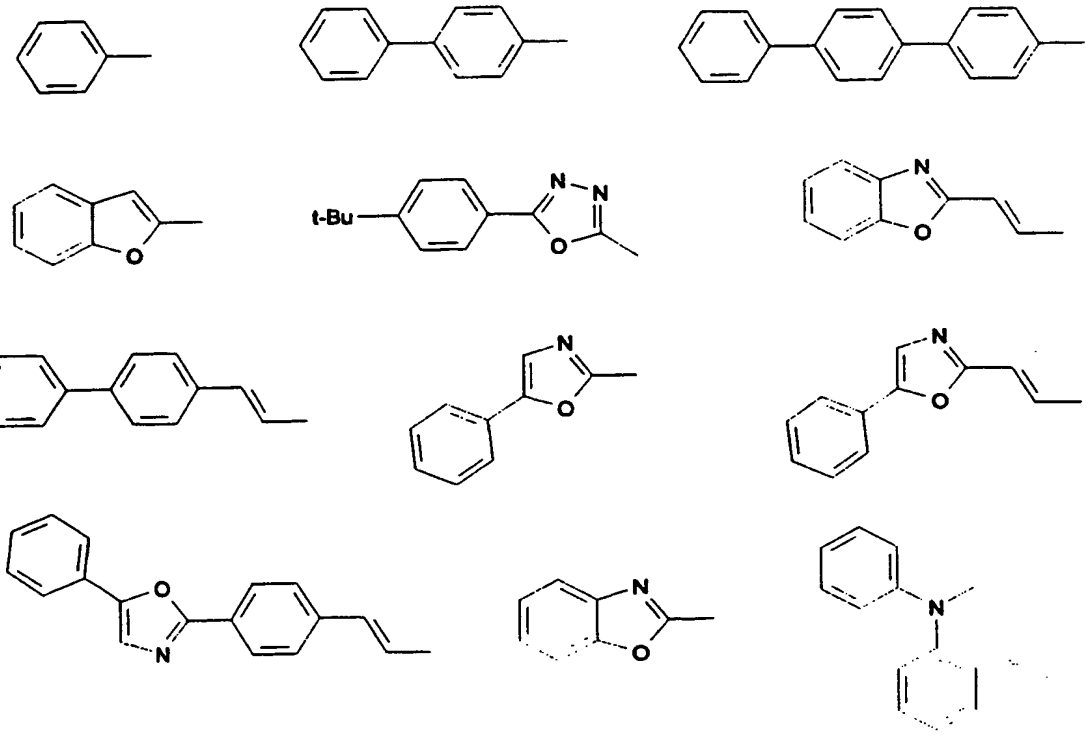
4. Use as claimed in one or more of claims 1 to 3, wherein use is made of a spirobifluorene derivative of the formulae (IIIa) to (IIIg)

IIIa) $K^{\oplus} = L = M = N^{\oplus}$ and is selected from the group consisting of:

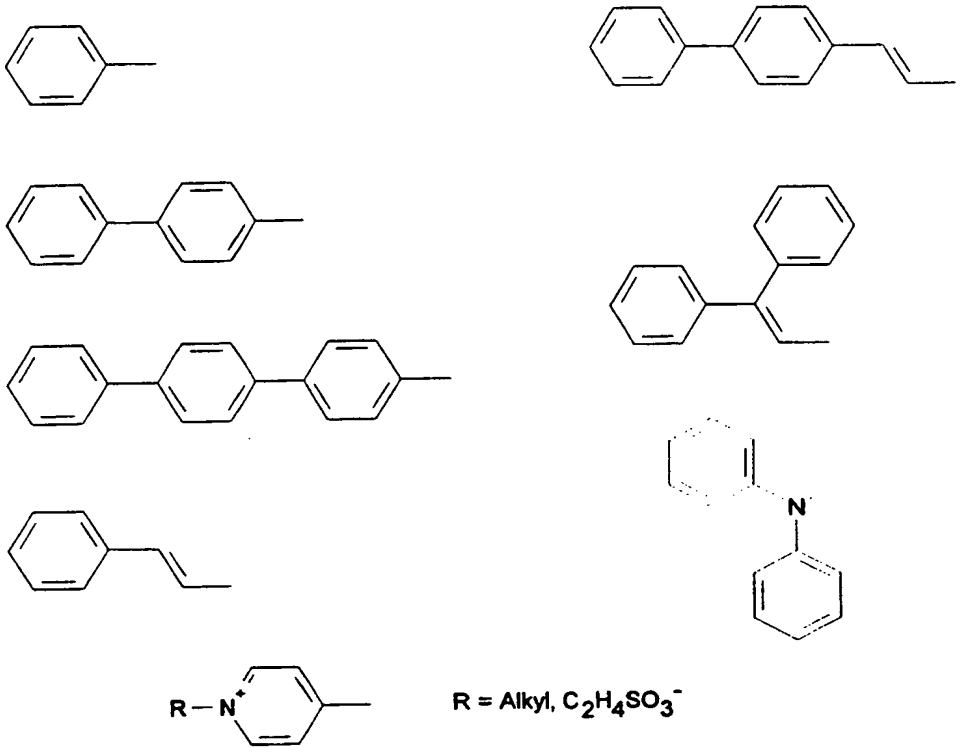


R = C_1-C_{22}-alkyl, $C_2H_4SO_3^-$

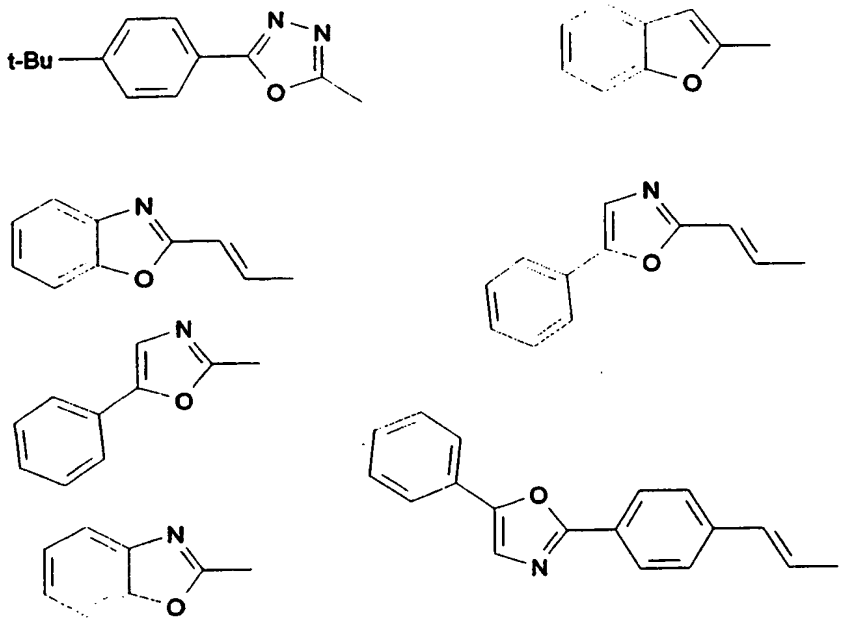
IIIb) $K^{\oplus}$ = M = H and $N^{\oplus}$ = L and is selected from the group consisting of:



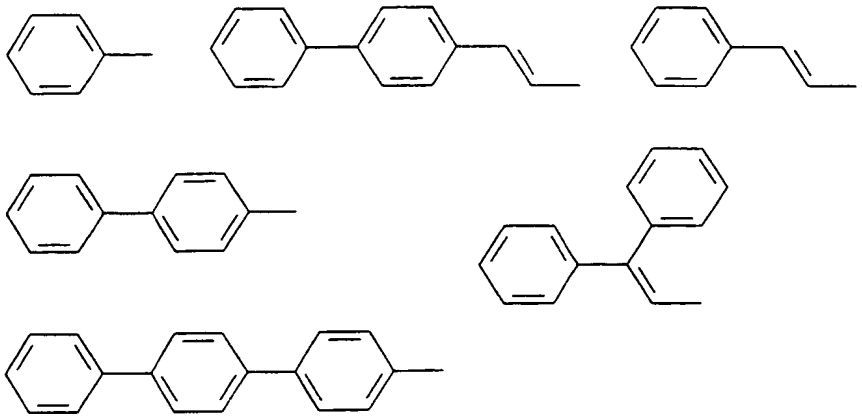
IIIc) K^a = M and is selected from the group consisting of:



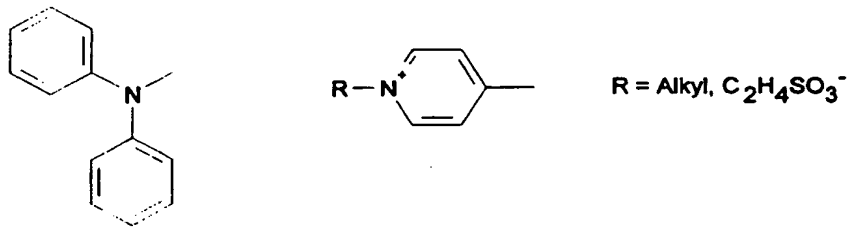
and N^a = L and is selected from the group consisting of:



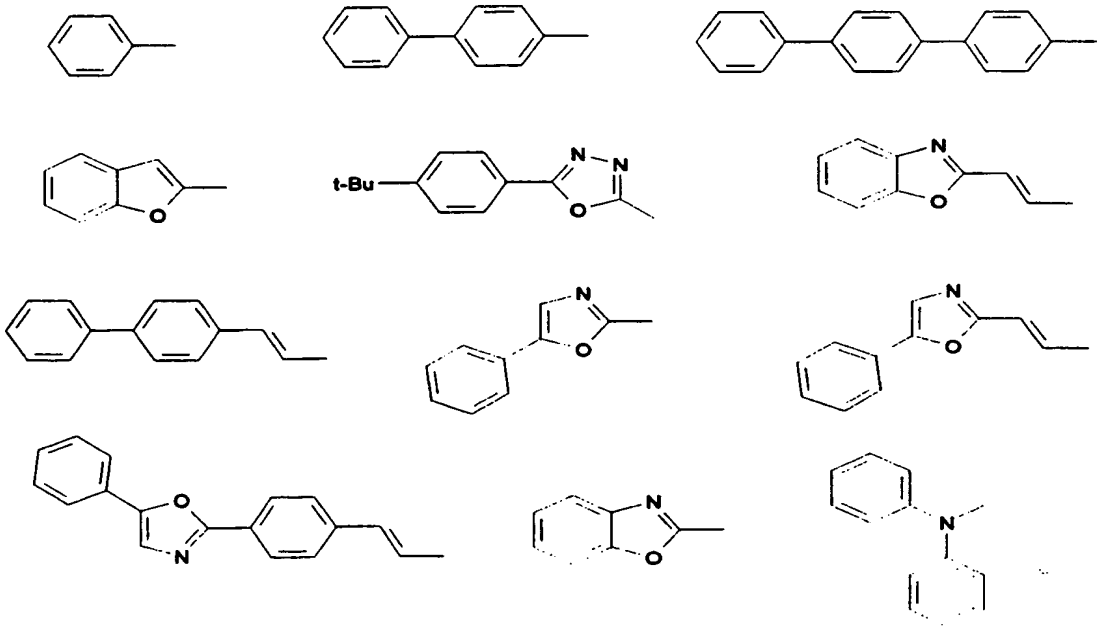
IIId) K^a = M and is selected from the group consisting of:



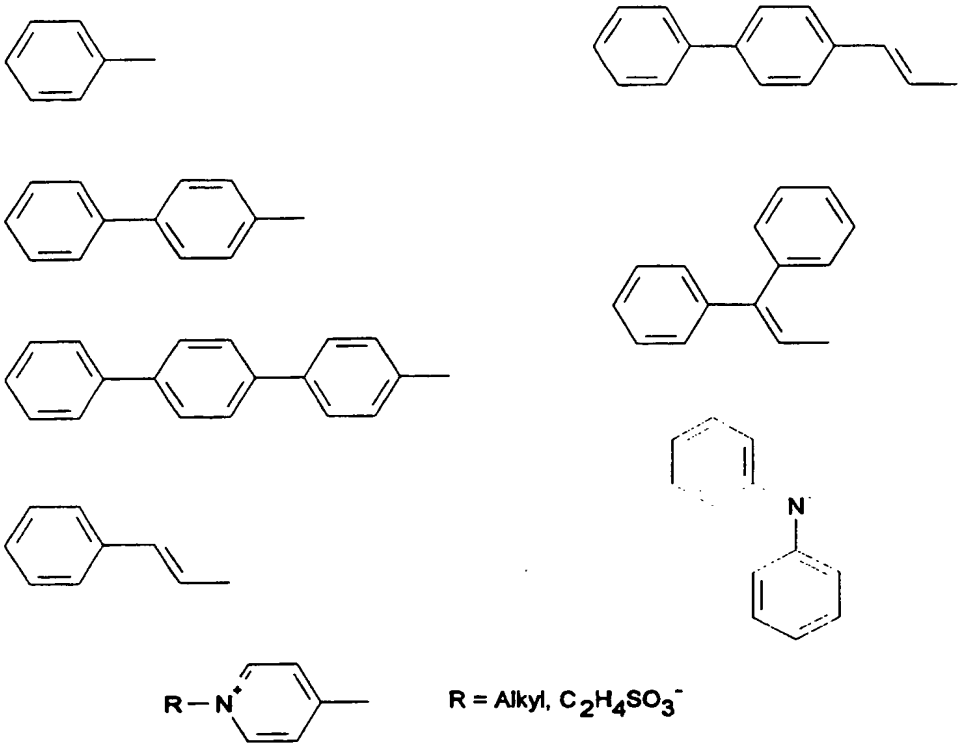
and N^a = L and is selected from the group consisting of:



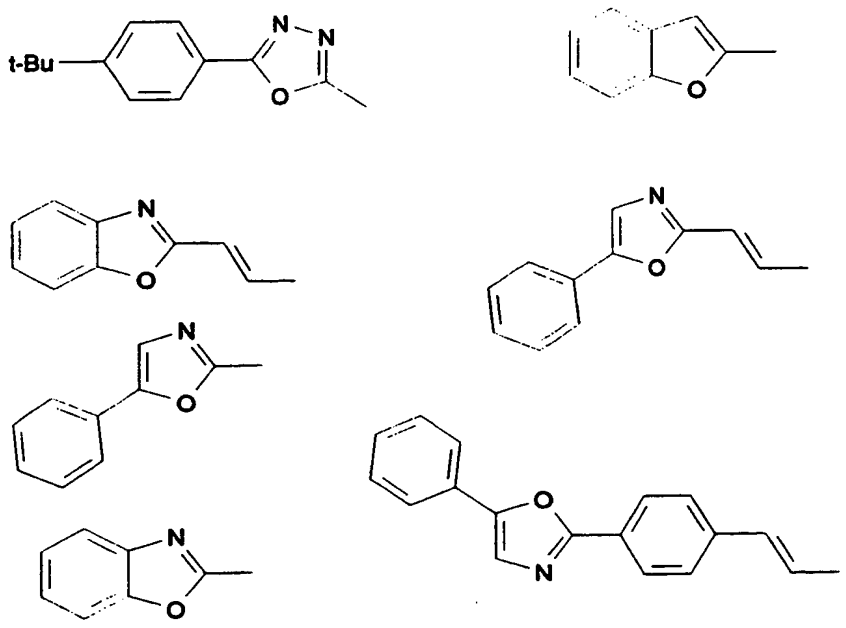
IIIe) K^a = L = H and M = N^a and is selected from the group consisting of:



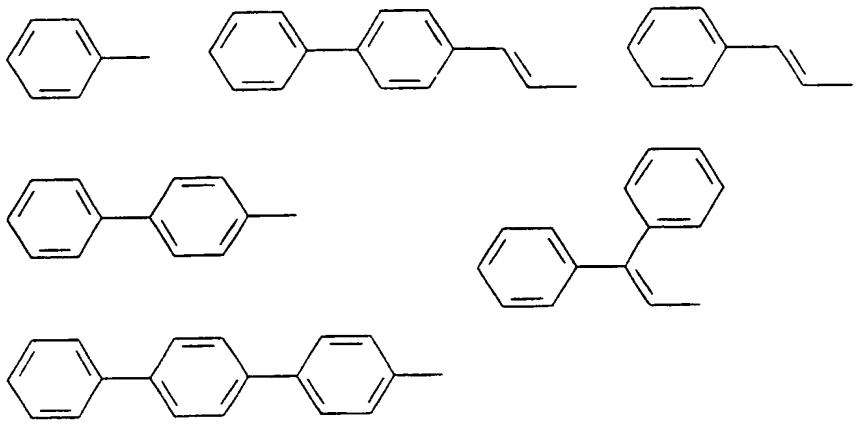
IIIf) K^a = L and is selected from the group consisting of:



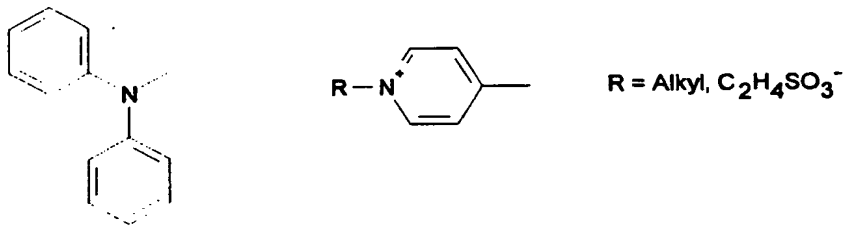
and M = N^a and is selected from the group consisting of:



IIIg) K^a = L and is selected from the group consisting of:

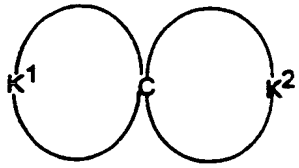


and M = N^a and is selected from the group consisting of:



Claims:

1. Use of spiro compounds of the formula (I)

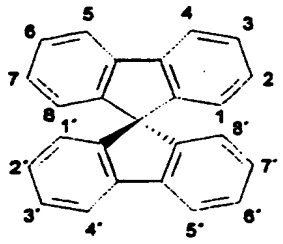


(I)

where

K^1 and K^2 are, independently of one another,conjugated systems, as a laser dye.

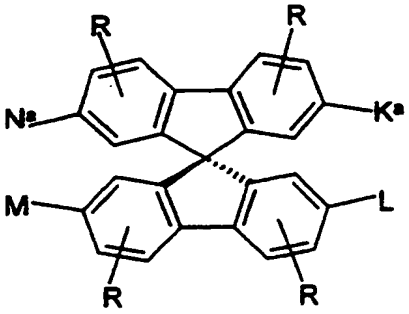
2. Use as claimed in claim 1, wherein the spiro compound used is a spirobifluorene of the formula (II)



(II)

where the benzo groups can be substituted and/or fused independently of one another.

3. Use as claimed in claim 1 and/or 2, wherein use is made of a spirobifluorene derivative of the formula (III)



(III)

where the symbols and indices have the following meaning:

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/00441

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 H01S3/16 H01S3/213 C09B57/00 //C07C13/72

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 H01S C09B C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 676 461 A (HOECHST AG) 11 October 1995 see page 3, line 32 - line 57; claims 1-5 ---	1-4
Y	LIPHARDT B ET AL: "LASERFARBSTOFFE, I. BIFLUOROPHORE LASERFARBSTOFFE ZUR STEIGERUNG DES WIRKUNGSGRADES VON FARBSTOFF-LASERN LASER DYES, I. BIFLUOROPHORIC LASER DYES FOR INCREASE OF THE EFFICIENCY OF DYE LASERS" LIEBIGS ANNALEN DER CHEMIE, vol. 1981, no. 6, June 1981, pages 1118-1138, XP002030899 * abstract * --- -/--	1-4

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 May 1999	25/05/1999

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Ginoux, C

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SUTCLIFFE F K ET AL: "THE SYNTHESIS AND PROPERTIES OF DYES AND PIGMENTS CONTAINING A 9,9'-SPIROBIFLUORENE RESIDUE" JOURNAL OF THE SOCIETY OF DYERS AND COLOURISTS, vol. 94, no. 7, July 1978, pages 306-309, XP002030898 cited in the application * Experimental part *	1-4
A	US 5 149 807 A (HAMMOND PETER R ET AL) 22 September 1992 see column 1, line 16 - line 68; claims; examples	1-4
A	DE 37 03 065 A (EXCITON CHEMICAL CO) 20 August 1987 see claims 1-14,25-30; examples 1,2	1-4
A	US 3 781 711 A (DREXHAGE K ET AL) 25 December 1973 see column 3, line 48 - column 4, line 49; claims	1-4

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 99/00441

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		DE 4442063 A	30-05-1996
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		CN 1112951 A	06-12-1995
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		US 5037578 A	06-08-1991
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		FR 2202920 A	10-05-1974
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